a hardened filter paper or a funnel with a sintered glass disc, washed with water, and pressed in order to squeeze out most of the water. It is not necessary to wash it free from $SO_4^=$. For the subsequent step, the wet cake, weighing from 109–143 g., is used.

2-(4-Hydroxybenzoyl)-benzoic Acid.—The wet, yellow cake of "phenolphthalein oxime" is placed into a flask or a beaker of 500 ml., fitted with a stirrer and a thermometer. One-hundred ml. 5 *N* of sulfuric acid, prewarmed to 90–104°, is then added in such a way as to wash down any oxime adhering to the neck of the flask or the side of the beaker. The stirrer is started and the yellow slurry rapidly heated. Within three minutes after the temperature has reached 96–102°, a dark yellow solution is formed. After one to three minutes from this point on, the solution first becomes turbid and then crystals of the acid appear. The reaction mixture is stirred for an additional ten minutes at 97–103°, gradually becoming brown. After cooling to 20°, the sandy crystals of 2-(4-hydroxybenzoyl)-benzoic acid are filtered off and washed with three portions of 20 ml. of water. After drying at 100–120°, the acid, of moderate greenish yellow color, weighs from 22.1–23.0 g. and melts at 209–213° cor. (sl. dec.); (yield 91.3–95.0% based on the phenolphthalein).

If a purer product is required, 20 g. of the acid, 0.5 g. of decolorizing carbon (Norit-A) and 1 liter of water are refluxed for fifteen minutes, filtered through a preheated funnel and the filtrate cooled to 5°. From 18.0–18.4 g. of acid, which melts at 211–215° cor. (sl. dec.), is obtained. This purified acid dissolves in ethanol (1 g. in 20 ml.) with but faint yellow color; its solution in 0.1 *N* sodium hydroxide (0.2 g. in 20 ml.) is clear and either light yellowish or faintly red.

From the filtrate of the acid, together with 75 ml. of wash-water, there can be obtained, after neutralization with 80 ml. of 5 *N* sodium hydroxide and about 60 ml. of 20% sodium sulfite solution and subsequent extraction with ether, 8.6–9.6 g. of *p*-aminophenol (m. p. 182–187°).

Equally good yields are obtainable with batches from 0.5 to 1.0 mole of phenolphthalein.

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Habit Modification of Ammonium Oxalate Monohydrate Crystals During Growth from Solution

BY HARRY J. KOLB[1] AND JOSEPH J. COMER[2]

In a previous paper,[3] the habit modification of ammonium dihydrogen phosphate was described. Additional investigations on the habit modification of ammonium oxalate monohydrate are presented here.

Procedure.—Ammonium oxalate monohydrate crystals were grown in the large water-bath described previously.[3] Each of the tanks was filled with 7.5 liters of ammonium oxalate solution saturated at 40°. Two crystal seeds, about 0.3 sq. cm. in the *z*-plane and 2 cm. along the *z*-axis, were suspended in each tank and grown, as before, by reduction of the temperature in the thermostat until the seeds were 4-cm. long. The cations which were added to the saturated oxalate solution containing the growing crystals are the eight listed in Table I. The concentrations of the cations were 0.1 g./liter of solution. Modification tests were also made at the following concentrations of magnesium ion: 0.001, 0.005, 0.01, 0.03, 0.05, 1.0, 2.0, 5.0 g./liter.

Results.—The ammonium oxalate monohydrate crystals normally show the (001), (110) and (010) planes. The modifications of the growing crystal by the cations are listed in Table I, *i. e.*, development of (021), (110) and (111) planes.

TABLE I

Development of planes	Zn^{++}	Cu^{++}	Mg^{++}	Sc^{+++}	Co^{++}[a]	Ni^{++}[a]	Cd^{++}	Mn^{++}
(110)	+	0	0	0	0	0	+	+
(111)	+	+	+	+	0	0	0	0
(021)	+	+	+	+	+	+	0	0

[a] Crystal tapered toward *z*-axis, obscuring the identity of individual planes.

In the series of experiments using magnesium ion, the (021) and $(0\bar{2}1)$ planes became more fully developed as the metal ion concentration increased until the (001) plane was finally eliminated. At the magnesium ion concentration of 5 g./liter, the growth of the crystal seed was completely inhibited.

The habit modification may be due to adsorption of foreign metal ions at the crystal–solution interface. This adsorption with subsequent habit modification could be explained by the insolubility interpretation (oxalate in this case) suggested in the previous paper.[3]

The oxalate reticular densities of the crystal planes were calculated and found to be (110), 3.54; (010), 2.87; (111), 1.83; (021), 1.71; (001), 1.06. All are relative to the (011) plane as 1.00. Thus, the appearance of the (021) plane rather than the (011) plane could be accounted for by the density sequence. The removal of the (001) plane could also be explained. In cases where the (110) plane was not developed (given in the table), no growth was noted on either the (110) or (010) planes. The cessation of all growth at high foreign cation concentrations supports a strongly adsorbed ion interpretation. However, it must be stated that we have no direct evidence of an adsorbed metal ion layer.

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[3] Kolb and Comer, THIS JOURNAL, **67**, 894 (1945).

The Molecular Structure of Trimethyl Silicon Chloride

BY R. L. LIVINGSTON[1] AND L. O. BROCKWAY

The silicon–carbon bond distances have been determined in several compounds and found to be less than the value of 1.93 Å. obtained for tetramethyl silicon.[2] For example, in hexamethyl disilicon[3] and in SiC,[4] the silicon–carbon distance

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[2] L. O. Brockway and H. O. Jenkins, THIS JOURNAL, **58**, 2036 (1936).

[3] L. O. Brockway and N. R. Davidson, *ibid.*, **63**, 3287 (1941).

[4] Ewald and Hermann, "Structurbericht," Akademische Verlagsgesell., 1931, 146.

is 1.90 Å. while in dimethyl silicon dichloride[5] this distance is 1.83 Å. if one assumes a tetrahedral angle for carbon–silicon–carbon. Trimethyl silicon chloride affords an opportunity for further study of the effect of chlorine substitution and for the determination of the silicon–chlorine distance which has been shown to vary somewhat from one chlorosilane to another.

Electron diffraction photographs of trimethyl silicon chloride were prepared using samples provided by W. F. Gilliam[6] of the General Electric Research Laboratory and by E. L. Warrick of the Mellon Institute. An electron wave length of 0.0592 Å. and a camera distance of 102.6 mm. were used. The photographs give rise to the s_0 values listed in Table I and qualitatively resemble curves E and F of Fig. 1. The features on the photographs beyond $s = 13$ (with the exception of a peak at 18.5) cannot be measured with a satisfactory reproducibility although the qualitative appearance is quite definite. Unreliable measurements are enclosed in parentheses and are not used in the quantitative comparisons.

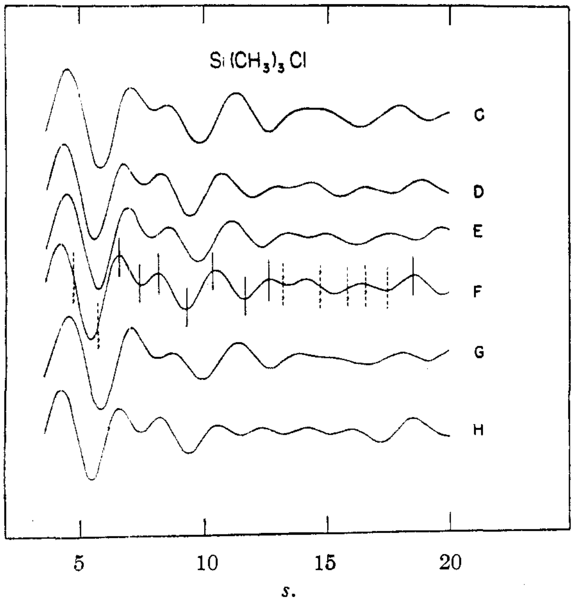

Fig. 1.—Theoretical electron scattering curves for trimethyl silicon chloride. The positions of the maxima and minima observed on the photographs are indicated by vertical lines.

TABLE I

CALCULATED AND OBSERVED DIFFRACTION MAXIMA FOR TRIMETHYL SILICON CHLORIDE

Max.	Min.	s_0	s_F/s_0	s_E/s_0
1		(4.76)		
	1	(5.71)		
2		6.53	1.006	1.060
	2	7.40	1.011	1.065
3		8.14	0.997	1.050
	3	9.30	0.995	1.048
4		10.34	1.012	1.075
	4	11.63	1.001	1.062
5		12.61	1.007	1.063
	5	(13.16)		
6		(14.70)		
	6	(15.80)		
7		(16.53)		
	7	(17.43)		
8		18.48	1.000	1.065
	8	(20.25)		
9		(21.57)		
	9	(22.87)		
10		(24.88)		
Average			1.004	1.061
Average deviation			0.005	0.006
Si-C, Å.			1.89	1.88
Si-Cl, Å.			2.09	2.08
∠C-Si-C, deg.			114	114

Scattering curves were calculated for the models shown in Table II. In all but model F the scale was fixed by a C–C distance of 2.96 Å.; the Si–Cl bond was assumed to lie on a trigonal axis of symmetry and C–H was set at 1.09 with ∠HCH = 109½°. Model F differs from E by a scale shift which fixes Si–C at 1.88 Å. and by having the trigonal axes of the methyl groups lie on the Si–C bonds. Of the calculated curves, only E and F agree qualitatively with the photographs. Models with Si–Cl/Si–C 1.07 or less (as in model C) fail to resolve the fifth and sixth maxima. This resolution is also poor in D which has the sixth peak too strong. Models with Si–Cl/Si–C 1.145 (as H) have the fourth maximum too weak or have one peak completely missing. In curve G the sixth maximum is almost completely missing.

TABLE II

CALCULATED MODELS FOR TRIMETHYL SILICON CHLORIDE

∠C-Si-C, deg.	(Si-Cl/Si-C)			
	1.030	1.070	1.105	1.145
109½	A	B	D	H
114		C	E, F	J
116			G	

The quantitative comparison for model E (Table I) leads to an s/s_0 ratio which is 6% greater than unity. Since C–H was chosen as 1.09 Å. in this model, this gives rise to somewhat large values for the distances between the hydrogens and other atoms. To check the effect of this on the final results, curves C, D, E, G and J were recalculated from models with the scale fixed by setting Si–C at 1.88 Å. and C–H = 1.09 Å. These curves do not differ qualitatively from the original ones and final quantitative results are based on F which gives results only slightly different from E. The final results are: Si–C = 1.89 ± 0.03 Å.; Si–Cl = 2.09 ± 0.03 Å. and ∠C–Si–C = 113 ± 2°.

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Discussion

The Si–Cl bond lengths in the chloromethyl silanes are: 2.09 ± 0.03 Å. in $Si(CH_3)_3Cl$, 1.99 ± 0.03 Å. in $Si(CH_3)_2Cl_2$,[5] 2.01 ± 0.02 Å. in $SiCH_3Cl_3$[5] and 2.02 ± 0.02 Å. in $SiCl_4$.[7] The distances in the chlorosilanes are (in the same order): 2.06 ± 0.05 Å.,[8] 2.02 ± 0.03 Å.,[7] 2.01 ± 0.03 Å.[9] and 2.02 ± 0.02 Å. In both series of compounds the chlorine bond is longer when only one chlorine is attached to the silicon than when two or more chlorine atoms occur in the same molecule. This observation is similar to the effect found in the C–F bonds in fluorocarbons, where the available data are far more extensive. On the basis of the Si–Cl distances reported we should expect the two monochlorosilanes to react more readily than the polychlorosilanes in reactions involving the removal of chlorine.

The Si–C distance reported in $Si(CH_3)_3Cl$ (1.89 ± 0.03 Å.) is intermediate between the values reported in $Si(CH_3)_4$ (1.93 ± 0.03 Å.) and in $Si(CH_3)_2Cl_2$ (1.83 ± 0.06 Å. with a regular tetrahedral angle assumed for C–Si–C).

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An Improved Synthesis of Glutaconic Ester

BY H. L. LOCHTE AND P. L. PICKARD[1]

Considerable quantities of glutaconic ester were required in connection with a synthetic problem, and previously described methods[2,3,4] were found tedious and expensive. A synthesis starting with citric acid was developed and found to give an over-all yield of 24%, based on the citric acid used. The citric acid was converted to acetonedicarboxylic ester, which was hydrogenated by Raney nickel to the hydroxy ester. This was dehydrated by thionyl chloride in pyridine. It was found that the hydrogenation either fails completely or proceeds very slowly except with a freshly prepared catalyst.

Diethyl Glutaconate.—One hundred grams of acetonedicarboxylic ester, prepared by the well-known method,[5] and about 1 g. of freshly prepared Raney nickel were hydrogenated at 1500 lb. pressure and 150°. Reduction was complete in four hours when the catalyst was very active, but in case of catalyst which had been stored under ethanol for long periods of time, or which had not been carefully prepared, hydrogenation either failed completely or was very slow. The catalyst was filtered off and discarded and the filtrate distilled at 2 mm. pressure. Seventy-seven grams (76%) of β-hydroxyglutaric ester was obtained, b. p. 105–107° (2 mm.), 133° (8 mm.), n^{20}_{D} 1.4381. This ester was dehydrated by the method of Gidvani[6] to yield 62 g. (88%) of glutaconic ester, b. p. 115° (4 mm.), n^{20}_{D} 1.4465. Saponification equivalent: found, 92.8; calculated, 93.1.

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The Standard Free Energy of Formation and Entropy of the Aqueous Magnesium Ion

BY C. C. STEPHENSON

Improved calculations of the standard free energy of formation and entropy of the aqueous magnesium ion are made possible by recent thermodynamic data concerning some magnesium compounds.

The standard free energy of solution of $MgCl_2 \cdot 6H_2O$ is given by the equation $\Delta F^\circ = -RT \ln 4(\gamma m)^3 a_1^6$, in which γ, the activity coefficient[1] of magnesium chloride in the saturated solution at 25° is 32.2, the solubility is 5.84 *m* and the activity of the water is 0.3296; hence, $\Delta F^\circ_{298.1} = -6,180$ cal. The free energies of formation of $MgCl_2 \cdot 6H_2O$,[2] H_2O and the chloride ion are −505,410 ± 320 cal., − 56,693 cal. and −31,340 cal., respectively; from these values and the standard free energy of solution, the standard free energy of formation of the aqueous magnesium ion at 25° is −108,760 cal. The corresponding electrode potential is 2.358 volts.

The standard heat of formation of the magnesium ion may be calculated from the heats of formation[3] of $Mg(NO_3)_2$ −188,770 cal., and $Mg(NO_3)_2 \cdot 6H_2O$, −624,410 cal., and the standard heats of solution,[4] −21,530 cal. and 4,340 cal., respectively. The heats of formation of the nitrate ion,[5] −49,320, and water, −68,318 cal., are consistent with the heats of formation of the solids. The heat of formation of the magnesium ion is −111,660 cal. calculated from the heat of formation and solution of $Mg(NO_3)_2$ and −111,520 cal. is obtained from the corresponding data for $Mg(NO_3)_2 \cdot 6H_2O$. With the latter value and the free energy of formation, $\Delta S^\circ_{298.1} = -9.3$ is calculated for the reaction $Mg + 2H^+ = Mg^{++} + H_2$, and the standard entropy of the magnesium ion is −32.7 cal. deg.$^{-1}$ mole^{-1}.

Additional values for the entropy and free energy of formation of the magnesium ion, derived from the solubility products of $Mg(OH)_2$, $MgCO_3$ and $Mg(NO_3)_2 \cdot 6H_2O$, are in good agreement, although less accurate. From a considera-

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