

Discussion

The Si-Cl bond lengths in the chloromethyl silanes are: 2.09 ± 0.03 Å. in $\text{Si}(\text{CH}_3)_3\text{Cl}$, 1.99 ± 0.03 Å. in $\text{Si}(\text{CH}_3)_2\text{Cl}_2$,⁵ 2.01 ± 0.02 Å. in $\text{SiCH}_3\text{-Cl}_3$ 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 $\text{Si}(\text{CH}_3)_3\text{Cl}$ (1.89 ± 0.03 Å.) is intermediate between the values reported in $\text{Si}(\text{CH}_3)_4$ (1.93 ± 0.03 Å.) and in $\text{Si}(\text{CH}_3)_2\text{Cl}_2$ (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

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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 acetone-dicarboxylic 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 acetone-dicarboxylic 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 dis-

carded 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 Gidvani⁶ 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

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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 $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ is given by the equation $\Delta F^\circ = -RT \ln 4(\gamma m)^2 a_1^6$, in which γ , the activity coefficient¹ 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, $\Delta F_{298.1}^\circ = -6,180$ cal. The free energies of formation of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$,² H_2O and the chloride ion are $-505,410 \pm 320$ 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 formation³ of $\text{Mg}(\text{NO}_3)_2$ $-188,770$ cal., and $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $-624,410$ 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 $\text{Mg}(\text{NO}_3)_2$ and $-111,520$ cal. is obtained from the corresponding data for $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. With the latter value and the free energy of formation, $\Delta S_{298.1}^\circ = -9.3$ is calculated for the reaction $\text{Mg} + 2\text{H}^+ = \text{Mg}^{++} + \text{H}_2$, 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 $\text{Mg}(\text{OH})_2$, MgCO_3 and $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, are in good agreement, although less accurate. From a considera-

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