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).

(7) L. O. Brockway and F. T. Wall, THIS JOURNAL, **56**, 2373 (1934).

(8) L. O. Brockway and I. E. Coop, *Trans. Faraday Soc.*, **34**, 1429 (1938).

(9) L. O. Brockway and J. Y. Beach, THIS JOURNAL, **60**, 1836 (1938).

CHEMISTRY LABORATORY
UNIV. OF MICHIGAN
ANN ARBOR, MICH.
RECEIVED FEBRUARY 12, 1946

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.), $n^{20}\mathrm{D}$ 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.), $n^{20}\mathrm{D}$ 1.4465. Saponification equivalent: found, 92.8; calculated, 93.1.

---

[1] General Aniline Fellow, 1944–1945.

[2] Conrad and Gutzeit, *Ber.*, **15**, 2841 (1882).

[3] Pechman and Jenisch, *ibid.*, **24**, 3250 (1891).

[4] Blaise, *Bull. soc. chim.*, [3] **29**, 1014, 1028 (1903).

[5] "Organic Syntheses," Coll. Vol. 1, **1941**, John Wiley and Sons, Inc., New York, N. Y., 10, 237.

[6] Gidvani, *J. Chem. Soc.*, 2666 (1932).

CHEMISTRY DEPARTMENT
THE UNIVERSITY OF TEXAS
AUSTIN, TEXAS
RECEIVED JANUARY 14, 1946

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-

[1] R. H. Stokes, *Trans. Faraday Soc.*, **41**, 642 (1945).

[2] K. K. Kelley and G. E. Moore, THIS JOURNAL, **65**, 2340 (1943).

[3] F. E. Young, *ibid.*, **66**, 773 (1944).

[4] W. W. Ewing, E. Klinger and J. D. Brandner, *ibid.*, **56**, 1053 (1934).

[5] W. R. Forsythe and W. F. Giauque, *ibid.*, **64**, 48 (1942).