652. *The Heat of Hydrolysis of Ethyl Orthosilicate and of Chlorotriethoxysilane.*

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The heat of hydrolysis at 25° c of ethyl orthosilicate in N-hydrochloric acid solution, and also in acetone–N-hydrochloric acid, has been measured. The heat of hydrolysis of chlorotriethoxysilane in water has been measured. From the heats of hydrolysis, the heats of formation have been derived :

$$\Delta H_f^\circ\ [\mathrm{Si(OEt)_4,\ liq.}] = -330{\cdot}2\ \text{kcal./mole, and}$$
$$\Delta H_f^\circ\ [\mathrm{Si(OEt)_3Cl,\ liq.}] = -291{\cdot}0\ \text{kcal./mole.}$$

These are based on the value $\Delta_f^\circ(\mathrm{SiO_2,2H_2O}) = -346{\cdot}2$ kcal./mole.

The heat of the gaseous redistribution reaction between ethyl orthosilicate and silicon tetrachloride to form chlorotriethoxysilane is calculated, $\Delta H_r = -4{\cdot}3$ kcal./mole of $\mathrm{Si(OEt)_3Cl}$.

Ogier [1] measured the heat of hydrolysis of ethyl orthosilicate in pure water, obtaining the value $-\Delta H_{\text{hyd.}} = 21{\cdot}6$ kcal./mole. He stated that the hydrolysis occurred rapidly, which would now suggest that his sample was impure. Thompson [2] has found that the pure substance hydrolyses very slowly in water, but much more rapidly in acid solutions. He reported a " preliminary " value of *ca.* 18 kcal./mole for $-\Delta H_{\text{hyd.}}$ in 0·1N-hydrochloric acid. We have found that the hydrolysis is very slow in pure water, reasonably rapid in N-hydrochloric acid, and fast in N-hydrochloric acid–acetone. The heat of hydrolysis of chlorotriethoxysilane has not previously been reported.

Both compounds are hydrolysed with the precipitation of silica; we have not investigated the precise nature of the precipitates. However, several authors have reported on the solid precipitates obtained on hydrolysis of ethyl orthosilicate, which appear to be hydrated silicas, $\mathrm{SiO_2,}x\mathrm{H_2O}$. Theissen and Koerner [3] isolated a number of distinct species, including $\mathrm{SiO_2,2H_2O}$, $\mathrm{2SiO_2,3H_2O}$, and $\mathrm{SiO_2,H_2O}$. The heats of decomposition of these into amorphous silica and water were found to be in the range 1·2—1·5 kcal./mole of $\mathrm{SiO_2}$. The value given in " Selected Values of Chemical Thermodynamic Properties " [4] for the heat of formation of the dihydrate is derived from the heat of decomposition (1·5 kcal./mole) of the dihydrate,[3] and a chosen value ΔH_f° ($\mathrm{SiO_2}$, amorphous) $= -202{\cdot}5$ kcal./mole. The latter, however, seems unsatisfactory in view of the recent finding by Humphrey and King [5] for the heat of combustion of pure silicon leading to ΔH_f° ($\mathrm{SiO_2}$, amorphous) $= 208{\cdot}1$ kcal./mole $\pm$ 0·3 kcal./mole. Accordingly, we have adopted the value ΔH_f° ($\mathrm{SiO_2,2H_2O}$) $= -346{\cdot}2$ kcal./mole in this work.

EXPERIMENTAL

Preparation of Compounds.—A sample of ethyl orthosilicate supplied by the Monsanto Chemical Company was distilled through an 18″ Fenske column, and the main fraction (b. p. 166·1° ± 0·1°/765 mm.) collected. This was redistilled through an 8″ gauze-packed column, and the fraction (b. p. 58·1° ± 0·2°/7 mm.) retained. Chlorotriethoxysilane was prepared according to the method of Schumb and Stevens,[6] by the controlled reaction between ethanol and silicon tetrachloride in ether. The product was purified by fractional distillation, and the main fraction redistilled through an 8″ gauze-packed column (b. p. 157·2° ± 0·2°/765 mm.).

Calorimeter.—The calorimeter, which has been previously described,[7] was immersed in a thermostat maintained at 25° c. The hydrolyses were carried out by breaking glass ampoules containing weighed amounts of reactant under the surface of the solvent in the Dewar vessel,

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[1] Ogier, *Ann. Chim. Phys.*, 1880, **20**, 5.

[2] Thompson, *J.*, 1953, 1908.

[3] Thiesson and Koerner, *Z. anorg. Chem.*, 1931, **197**, 307.

[4] Nat. Bureau Stands., Washington, Circular 500, 1952.

[5] Humphrey and King, *J. Amer. Chem. Soc.*, 1952, **74**, 2041.

[6] Schumb and Stevens, *ibid.*, 1947, **69**, 726.

[7] Skinner and Smith, *Trans. Faraday Soc.*, 1953, **49**, 601.

and following the ensuing temperature changes through the resistance changes of a shielded thermistor element immersed in the solution.

Units.—The calorimeter was calibrated electrically by the substitution method. Heat quantities are given in thermochemical calories, 1 cal. = 4·1840 abs. joules.

Results.—(1) *Ethyl orthosilicate.* The first series of experiments were carried out with 500 ml. of N-hydrochloric acid in the Dewar vessel. The hydrolyses required *ca.* 15 min. for completion, and the ethyl orthosilicate tended to float on the acid solution. A second series of experiments used a mixture of 320 ml. of acetone and 160 ml. of N-hydrochloric acid; in this, hydrolysis was rapid, and the orthosilicate did not float. Silica was precipitated in both sets of experiments, and we have presumed this to be the dihydrate, $SiO_2,2H_2O$.

The observed heats of hydrolysis, $\Delta H_{obs.}$, are listed in Table 1. The heats refer to the processes:

$$(1)\ Si(OEt)_4\ (liq.) + nHCl(55H_2O) \longrightarrow SiO_2,2H_2O\ (ppt.) + [4EtOH + nHCl]\ in\ [55n - 4]H_2O$$

and

$$(2)\ Si(OEt)_4\ (liq.) + mHCl(55H_2O,22C_3H_6O) \longrightarrow SiO_2,2H_2O\ (ppt.) + [4EtOH + mHCl + 22C_3H_6O]\ in\ [55m - 4]H_2O$$

The column headed $\Delta H_{hyd.}$ gives the heats (derived from $\Delta H_{obs.}$ on correction for the heat of solution of ethyl alcohol in the solvents used) of the idealized hydrolysis: $Si(OEt)_4\ (liq.) + 4H_2O\ (liq.) \longrightarrow SiO_2,2H_2O\ (ppt.) + 4EtOH\ (liq.)$. The solution heat correction terms were measured separately, viz:

(*a*) solution of ethyl alcohol in N-hydrochloric acid, $\Delta H_{soln.} = -2{\cdot}15$ kcal./mole of ethyl alcohol

and (*b*) solution of ethyl alcohol in the acetone–N-hydrochloric acid, $\Delta H_{soln.} = 0{\cdot}28$ kcal./mole of ethyl alcohol.

TABLE 1. *Heat of hydrolysis of ethyl orthosilicate.*

(Expts. 1—7 were in N-hydrochloric acid; Expts. 8—10 in acetone–hydrochloric acid.)

Expt.	Wt. (g.)	n	$-\Delta H_{obs.}$ (kcal./mole)	$-\Delta H_{hyd.}$ (kcal./mole)	Expt.	Wt. (g.)	n	$-H_{obs.}$ (kcal./mole)	$-\Delta H_{hyd.}$ (kcal./mole)
1	1·2177	85	16·85	8·25	6	1·0045	104	17·09	8·49
2	1·1192	93	16·83	8·23	7	1·4538	72	16·98	8·38
3	1·1672	89	16·73	8·13	8	0·9570	35	6·96	8·08
4	2·0357	51	16·62	8·02	9	1·2871	26	7·11	8·23
5	1·1018	94	16·55	7·95	10	1·3070	26	6·89	8·01
								Mean:	8·20 ± 0·2

TABLE 2. *Heat of hydrolysis of chlorotriethoxysilane.*

Expt.	Wt. (g.)	% purity (Cl analysis)	Total cals., obs.	cals. from $Si(OEt)_4$	$-\Delta H_{corr.}$ (kcal./mole)
1	1·2874	97·7	183·7	2·6	28·6
2	1·1127	95·7	155·3	4·2	28·2
3	1·0524	94·6	149·0	4·9	28·7
4	1·0418	94·8	156·1	4·7	28·4
5	0·9614	95·5	135·2	3·8	28·4
6 *	0·9862	82·1	132·6	15·4	28·7 *
7 *	1·3511	66·1	168·4	40·0	28·6 *
				Mean:	28·5 ± 0·2

* Runs 6 and 7: ethyl orthosilicate was added to the sample. The corrections for the heat of hydrolysis of the orthosilicate impurity were based on $-\Delta H = 18{\cdot}2$ kcal./mole of ethyl orthosilicate. This value differs from that in Table 1, since the heat of solution of ethyl alcohol is larger in dilute (*ca.* 0·01N) than in N-hydrochloric acid.

(2) *Chlorotriethoxysilane.* Chlorotriethoxysilane hydrolyses easily in water, and all the experiments were made with 500 ml. of distilled water in the calorimeter. Aliquot samples from the final solutions were titrated for hydrochloric acid against N/40-sodium hydroxide, and for chloride ion by Volhard's method. The analyses showed that the chlorotriethoxysilane was contaminated slightly, since the chlorine content was found generally to be low (95—98%): Schumb and Stevens [6] similarly observed that the chlorine content of their preparation was a few units % low. The impurity is very likely to be ethyl orthosilicate, and microanalysis of

the sample for carbon and hydrogen supported this. The observed heats of hydrolysis were corrected on the assumption that the impurity was ethyl orthosilicate. In some experiments, the chlorotriethoxysilane was deliberately diluted with ethyl orthosilicate in order to check that the corrections were properly applied. The values given under $\Delta H_{\text{corr.}}$ in Table 2 relate to the reaction :

$$\mathrm{Si(OEt)_3Cl\ (liq.)} + (n + 4)\mathrm{H_2O\ (liq.)} \longrightarrow \mathrm{SiO_2,2H_2O\ (ppt.)} + (3\mathrm{EtOH} + \mathrm{HCl})\ \text{in}\ n\mathrm{H_2O\ (soln.)}$$

Values of n varied from 3700 to 6000.

DISCUSSION

From the mean values of $\Delta H_{\text{hyd.}}$ (Table 1) and ΔH_{corr} (Table 2), together with certain known heats of formation, we may derive values for the heats of formation of liquid ethyl orthosilicate and of liquid chlorotriethoxysilane. Using the following data,[4] $\Delta H_f{}^\circ$ (H_2O, liq.) = 68·32 kcal./mole, $\Delta H_f{}^\circ$ (EtOH, liq.) = −66·36 kcal./mole, $\Delta H_f{}^\circ$ (HCl, aq.) = −39·97 kcal./mole, $\Delta H_f{}^\circ$ (EtOH, aq.) = −68·85 kcal./mole, and the value for $\Delta H_f{}^\circ$ ($SiO_2,2H_2O$, ppt.) discussed earlier, we derive :

$$\Delta H_f{}^\circ\ [\mathrm{Si(OEt)_4,\ liq.}] = -330{\cdot}2\ \text{kcal./mole and}\ \Delta H_f{}^\circ\ [\mathrm{Si(OEt)_3Cl,\ liq.}] = -291{\cdot}0\ \text{kcal./mole.}$$

Although the calorimeter errors in the heats of hydrolysis are small, lying within limits of less than $\pm \frac{1}{2}$ kcal./mole, the absolute errors attached to the derived $\Delta H_f{}^\circ$ values may be significantly larger. The main difficulty in assessing these arises from our assumption that the silica formed on hydrolysis is precipitated *in toto* as dihydrate. It is possible that part of the silica formed remained in colloidal solution. Roth and Schwartz,[8] and also Chernick,[9] observed from studies on the heat of hydrolysis of silicon tetrachloride in water at room temperature that silica was not precipitated under the conditions they used, but remained entirely in colloidal solution. In the present hydrolysis experiments, the amount of silica remaining in solution was not determined, although it was probably small as judged by the bulk of precipitated silica formed. Nevertheless, this weakness in the present study remains, and the overall error limits in the derived $\Delta H_f{}^\circ$ values may amount to ± 2 kcal./mole in consequence.*

It was originally intended to measure the heats of hydrolysis of each compound belonging to the group $\mathrm{Si(OEt)_{4-n}Cl_n}$ (n = 0—4) in order to examine the degree of constancy of the Si–Cl and Si–OEt bond energy term values within this group (*cf.* the similar studies by Skinner and Smith on the group of dimethylaminochloroborines [10] and ethoxychloroborines [11]). We have not completed this programme partly because of the difficulty of preparing the compounds in a satisfactory state of purity, and also because of the thermochemical uncertainties attendant upon partial precipitation of silica. The study by Chernick of the heat of hydrolysis of silicon tetrachloride confirmed the result obtained by Roth and Schwartz, and leads to the value $\Delta H_f{}^\circ$ ($SiCl_4$,liq.) = −156·4 kcal./mole. Accepting the values $\Delta H_{\text{vap.}}$ = 7·0 kcal./mole [4] for the heat of vaporization of silicon tetrachloride, and $\Delta H_{\text{vap.}}$ = 10·0 kcal./mole [2] for the heat of vaporization of ethyl orthosilicate, and interpolating between these to derive $\Delta H_{\text{vap.}}$ ~9·2 kcal./mole for the heat of vaporization of chlorotriethoxysilane, we obtain −149·4, −320·2, and −281·8 kcal./mole, respectively, for the heats of formation of these compounds in their gaseous states. Hence, we may calculate the heat of the gaseous redistribution reaction : [12]

$$\tfrac{3}{4}\mathrm{Si(OEt)_4} + \tfrac{1}{4}\mathrm{SiCl_4} \longrightarrow \mathrm{Si(OEt)_3Cl}$$

and obtain ΔH_r = −4·3 kcal./mole. It is admitted that the overall uncertainties in the heat of formation values are too large to allow much reliance to be put on this derived

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* If as much as 50% of the total silica remained in solution in the experiments made with ethyl orthosilicate, a correction of 1·5 kcal./mole would be necessary, giving $\Delta H_f{}^\circ$ = − 328·7 as opposed to −330·2 kcal./mole.

[8] Roth and Schwartz, *Z. phys. Chem.*, 1928, **134**, 456.

[9] Chernick, unpublished work.

[10] Skinner and Smith, *J.*, 1954, 2324.

[11] *Idem, ibid.*, p. 3920.

[12] Skinner, *Rec. Trav. chim.*, 1954, **73**, 991.

heat of redistribution; nevertheless, it is of interest that the redistribution heat is apparently of similar magnitude and sign to those measured by Skinner and Smith [11] in the group of chloroethoxyborines.

Tanake and Watase [13] recently reported on their measurements of the heat of combustion of liquid methyl orthosilicate, from which they derived the value ΔH_f° [$Si(OMe)_4$, liq.] $= 300$ kcal./mole. Thus, the increment in the heat of formation in passing from methyl to ethyl orthosilicate is *ca.* —30 kcal./mole, or —7·5 kcal./mole per CH_2 group. This is rather low by comparison with the CH_2 increments in passing from MeOH to EtOH, $B(OMe)_3$ to $B(OEt)_3$, $As(OMe)_3$ to $As(OEt)_3$, and $P(OMe)_3$ to $P(OEt)_3$, in which [14,15,16] the increments are *ca.* —9 kcal./mole per CH_2 group.

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[13] Tanake and Watase, *J. Chem. Phys.*, 1954, **22**, 1268.
[14] Charnley, Skinner, and Smith, *J.*, 1952, 2288.
[15] Charnley, Mortimer, and Skinner, *J.*, 1953, 1181.
[16] Chernick, Skinner, and Mortimer, *J.*, 1955, 3936.