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CALORIMETRIC DETERMINATION OF THE HEAT OF REACTION OF SOLID TRIS(HYDROXYMETHYL)AMINOMETHANE WITH 0.1 *M* HCl SOLUTIONS AT 10, 25 AND 40°C*

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ABSTRACT

The heat of reaction of solid tris(hydroxymethyl)aminomethane (THAM) with 0.1 *M* hydrochloric acid solution has been determined calorimetrically at 10, 25, and 40°C. The experimental conditions suggested by the Standards Committee of the U.S. Calorimetry Conference were followed. Values of ΔH° of -7.644 ± 0.014, -7.104 ± 0.008, and -6.555 ± 0.012 kcal/mole at 10, 25, and 40°C, respectively, are reported. Results of the study are compared with those of other workers, and THAM is recommended for use as an interlaboratory comparison standard for solution calorimetry.

INTRODUCTION

There is a definite need for a suitable reaction which could be used as an interlaboratory comparison standard for solution calorimetry. The principal purpose of such a comparison standard would be to eliminate systematic errors sometimes associated with new equipment or with changes made to existing apparatus. The requirements for this kind of comparison standard as outlined by Gunn[1] are sufficiently numerous and demanding as to exclude most materials from even a cursory consideration. A few reactions, however, which meet most or all of the requirements, have been reported.

The heat of solution of KCl has been frequently suggested, but the reported[2] values differ by as much as 1% from one another, and both Gunn[1] and Sunner and Wadsö[3] have concluded that the system is unsatisfactory. The heat of neutralization of a strong base with a strong acid also has been recommended as a possible comparison standard. The heat of neutralization of $HClO_4$ with NaOH, for example, has been proposed as a comparison standard[4] but does not meet certain of the requirements outlined by Gunn, such as being nonreactive with the atmosphere and having a small temperature coefficient. On the basis of work by Gunn[1], the heat of neutraliza-

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tion of H_2SO_4 with excess NaOH appears to be excellent for comparing calorimeters in the same laboratory, since the reproducibility for the same batch of H_2SO_4 is very good. However, the reproducibility between batches of H_2SO_4 is no better than between batches of the solid compound known as THAM [tris(hydroxymethyl)-aminomethane or 2-amino-2-(hydroxymethyl)-1,3-propanediol] which the Standards Committee of the U.S. Calorimetry Conference has been investigating as a possible interlaboratory comparison standard. Other things being equal, the advantages of being able to work with a non-corrosive solid are obvious. THAM has already found use as a primary acidimetric standard and appears to meet the majority of the requirements for a solution calorimetry standard. The heat of reaction of THAM(s) with an HCl solution is a combination of the endothermic heat of solution and the exothermic heat of protonation of THAM, the overall reaction being exothermic. The protonation reaction is given by Eqn. (1).

$$(HOCH_2)_3CNH_2 + H^+ = (HOCH_2)_3CNH_3^+ \quad (1)$$

It should be noted that there is no change in the ionic strength of the solution during the reaction.

At the suggestion of the Standards Committee of the U.S. Calorimetry Conference[5], several laboratories including ours agreed to accept samples of THAM prepared by the National Bureau of Standards (NBS) for the purpose of determining the heat of reaction of THAM(s) with HCl using certain specified experimental conditions among which the principal ones are: (a) the reaction temperature should be 25.00 °C, (b) the concentration of THAM should be 5 g/l, (c) the concentration of the HCl solution should be 0.100 mole/l, (d) the NBS sample of THAM should be stored with no further crushing or grinding in an atmosphere of 50% relative humidity, weighed in air, and sealed in a glass ampoule at atmospheric pressure, and (e) a blank determination should be made. These conditions were followed in this study. Values for the heat of reaction of THAM(s) with 0.100 *M* HCl at 10, 25, and 40 °C are reported here together with a summary of published results from other laboratories.

EXPERIMENTAL

Materials. — Reagent grade hydrochloric acid (Dupont) and double-distilled, freshly boiled H_2O were used to prepare a stock solution of 0.10035 *M* HCl. This solution was standardized with THAM (Fisher Cerified Reagent, lot no. 772419, assay 99.9%) and then checked with standard sodium hydroxide solutions using in each case a pH meter to detect end points.

The THAM used in the heat of reaction measurements was that prepared by the National Bureau of Standards and labeled "NBS Standard Reference Material 724, Solution Calorimetry Standard". The stated purity was 99.94±0.01%. This sample was spread in a thin layer on a watchglass and stored at 25 °C in a desiccator over a saturated magnesium nitrate solution which provides an atmosphere of about 50% relative humidity.

Apparatus and thermistor calibration. — These have been described in refs. 4 and 6.

Procedure. — Samples of THAM (approximately 0.877 g) were weighed in air and sealed with Parafilm at atmospheric pressure in thin-walled glass ampoules of about 10 ml volume. For comparison, some ampoules were carefully sealed with a flame. Each ampoule, attached to a rod within the calorimeter, was broken into 175 ml of 0.1 *M* HCl solution, thus providing a THAM concentration in the final solution of 5 g/l. The initial temperatures were 10.000±0.005 °C, 25.000±0.005 °C, and 40.000±0.005 °C for the runs at 10, 25, and 40 °C, respectively. The balance of the procedure followed was the same as previously described[6]. Blank determinations showed the heat effect due to breaking the ampoule to be <0.1%. This heat effect was assumed to be negligible in comparison to the total heat evolved in the reaction.

Calculations. — In Tables I, II, and III are given the data necessary for calculating the heat of reaction of THAM(s) with HCl solutions at 10, 25, and 40 °C, respectively. The heats of reaction at 10 and 40 °C were calculated as described previously[6]. At 25 °C, however, the simplified equation suggested by Skinner *et al.*[7] was used. This equation has the form

$$T_2 - T_1 = A \log (R_1/R_2) \tag{2}$$

in which each symbol has the meaning previously indicated[6], and *A* is a constant which cancels out during the calculations. The specific equations used were:

$$\Delta T_r = A \log (R_{T_1}/R_{T_2}) \tag{3}$$

$$\Delta T_c = A \log (R_{H_1}/R_{H_2}) \tag{4}$$

$$Q_c = E_{htr} \cdot E_{std} \cdot k \cdot t \tag{5}$$

$$Q_r = -Q_c(\Delta T_r/\Delta T_c) \tag{6}$$

Corrections were made in the measured heat for condensation and vaporization as suggested by Gunn[1]. The condensation correction, Q_{cond}, which is exothermic, was calculated from Eqn. (7) and is the heat of condensation of the water removed from the vapor space in the reaction vessel due to changes in vapor pressure above the aqueous phase.

$$Q_{cond} = H_{vap} \cdot V_v(P_w - P_s)/P_w \tag{7}$$

In these equations H_{vap} is the heat required to saturate 1 ml of vapor space with water, V_v is the volume of the vapor space in the reaction vessel, P_w is the vapor pressure of water, P_s is the vapor pressure of the THAM solution and the term $(P_w - P_s)/P_w$ is equal to 0.00015*c* in which *c* is the concentration of THAM in g/l. The calculated condensation corrections were found to have typical values of 0.00023, 0.00055, and 0.00120 cal at 10, 25, and 40 °C, respectively,

TABLE I

VALUES OF Δ*H* FOR THE REACTION OF THAM(s) WITH HCl AT 10°C

Run no.	C_p *(cal/deg)*	Q_o *(cal)*	T_r *(°C)*	Q_r (cal)	*Weight of THAM (in vacuo) (grams)*	*Concentration of THAM (grams/liter)*	*Corrections*[a] *(calculated) (cal)*		*Heat of reaction* Δ*H* *(corrected by Blank)*	
							Q_{vap}	Q_{cond}	*(Joules/gram)*	*(kcal/mole)*
1	−183.06	−11.785	0.3034	−55.541	0.8774	5.006	0.0	−0.00024	−264.3	−7.652
2	−182.25	−46.083	0.3042	−55.432	0.8778	5.008	0.0	−0.00024	−263.7	−7.634
3	−181.53	−29.747	0.3063	−55.605	0.8774	5.005	0.0	−0.00023	−264.6	−7.661
4	−181.07	−29.105	0.3059	−55.396	0.8763	4.999	0.0	−0.00023	−263.9	−7.642
5	−182.06	−31.842	0.3041	−55.367	0.8765	5.000	0.0	−0.00024	−263.7	−7.636
6	−181.60	−25.771	0.3062	−55.607	0.8765	5.000	0.0	−0.00023	−264.9	−7.670
7	−182.61	−31.359	0.3023	−55.201	0.8764	5.000	0.0	−0.00024	−263.0	−7.614
8[b]	−181.88	−11.563	0.0006	−0.115						
								average	−264.0±0.5	−7.644±0.014

[a] See Eqns. 7 and 9.

[b] Blank for runs 1–7.

TABLE II

VALUES OF ΔH FOR THE REACTION OF THAM(s) WITH HCl AT 25°C.

Run no.	C_p *(cal/deg)*	Q_o *(cal)*	ΔT_r *(°C)*	Q_r *(cal)*	*Weight of THAM (in vacuo) (grams)*	*Concentration of THAM (grams/liter)*	*Corrections*[a] *(calculated) (cal)*		*Heat of reaction* ΔH *(corrected by Blank)*	
							Q_{vap}	Q_{cond}	*(joules/gram)*	*(kcal/mole)*
17	−181.45	−33.581	0.2826	−51.279	0.8767	5.000	0.055	−0.0005	−244.9	−7.091
18	−181.82	−33.222	0.2821	−51.291	0.8766	5.000	0.055	−0.0006	−245.0	−7.093
19	−182.75	−30.738	0.2809	−51.335	0.8768	5.000	0.055	−0.0005	−245.2	−7.098
20	−181.56	−36.532	0.2831	−51.399	0.8767	5.000	0.055	−0.0006	−245.5	−7.108
21	−181.25	−34.447	0.2834	−51.367	0.8768	5.001	0.055	−0.0005	−245.3	−7.103
22	−181.11	−33.688	0.2835	−51.346	0.8767	5.000	0.055	−0.0006	−245.2	−7.100
23	−182.02	−25.584	0.2831	−51.531	0.8767	5.000	0.055	−0.0005	−246.1	−7.126
24	−181.21	−33.328	0.2837	−51.410	0.8768	5.000	0.055	−0.0006	−245.5	−7.109
25[b]	−180.73	−22.194	−0.0003	0.041						
								average	−245.3 ± 0.3	−7.104 ± 0.008

[a] See Eqns. 7 and 9.

[b] Blank for runs 17–24.

TABLE III

VALUES OF ΔH FOR THE REACTION OF THAM(s) WITH HCl AT 40 °C

Run no.	C_p *(cal/deg)*	Q_0 *(cal)*	ΔT_r (°C)	Q_r *(cal)*	*Weight of THAM (in vacuo) (grams)*	*Concentration of THAM (grams/liter)*	*Corrections*[a] *(calculated) (cal)*		*Heat of reaction* ΔH *(corrected by Blank)*	
							Q_{val}	Q_{cond}	*(Joules/gram)*	*(kcal/mole)*
9	−181.31	−39.088	0.2609	−47.297	0.8771	4.998	0.241	−0.0012	−227.0	−6.572
10	−180.39	−32.000	0.2614	−47.147	0.8769	4.997	0.241	−0.0012	−226.3	−6.552
11	−181.13	−31.936	0.2597	−47.033	0.8770	4.998	0.241	−0.0012	−225.7	−6.536
12	−180.52	−30.527	0.2607	−47.059	0.8770	4.998	0.241	−0.0012	−225.9	−6.540
13	−180.77	−31.942	0.2622	−47.405	0.8771	4.998	0.171	−0.0012	−226.7	−6.562
14	−181.96	−32.102	0.2608	−47.455	0.8771	4.999	0.171	−0.0012	−226.9	−6.568
15[b]	−177.55	−13.832	−0.0016	0.284						
16[c]	−177.79	−17.251	−0.0006	0.105						
								average	−226.4 ± 0.4	−6.555 ± 0.012

[a] See Eqns. 7 and 9. [b] Blank for runs 9–12. [c] Blank for runs 13–14.

The vaporization correction, Q_{vap}, which is endothermic, was calculated from Eqns. (8) and (9) and is the heat of vaporization of that amount of water necessary to saturate the air in the sample ampoules.

$$V_f = V_b - m/1.35 \qquad (8)$$

$$Q_{vap} = H_{vap}\, V_f(1-r) \qquad (9)$$

In these equations, V_f is the free volume of the sample ampoule, V_b is the total internal volume of the sample ampoule in milliliters, m is the mass of the sample in grams, 1.35 is the density of THAM in grams/cm^3, H_{vap} has the same meaning as in Eqn. (7) and r is the relative humidity of the air in the sample bulb (*i.e.*, the absolute humidity of the air in the balance room converted to relative humidity at the temperature of measurement). The calculated corrections for vaporization were 0.000, 0.055, and 0.215 cal at 10, 25, and 40 °C, respectively.

The condensation and vaporization corrections were small and negligible except for the correction for vaporization at 40 °C but were evaluated in each case as suggested by the Standards Committee[4].

RESULTS

Experimental data and ΔH values obtained in this study for the reaction of THAM(s) with HCl solution are given in Tables I, II, and III.

The value determined in this study for the heat of reaction at 25 °C of THAM(s) with HCl solution agrees to ±0.1% with previously reported values at this temperature and under similar experimental conditions.

The values obtained in this study for the heat of reaction at 10, 25, and 40 °C of THAM(s) with HCl solution together with other reported values including those at 0, 15, 25, and 50 °C reported recently by Hill *et al.*[8] are listed in Table IV. The

TABLE IV

HEAT OF REACTION OF THAM(s) WITH 0.100 *M* HCl AT VARIOUS TEMPERATURES

Temperature	$-\Delta H$ (*kcal/mole*)
0	8.112[8]
10	7.644 (this study)
15	7.524[8]
20	7.306[9]
25	7.104 (this study), 7.109[8], 7.104[9] 7.111[10], 7.112[11], 7.1070[1] 7.109[12], 7.123[13], 7.125[14] 7.114[15]
30	6.904[9]
40	6.555 (this study)
50	6.055[8]

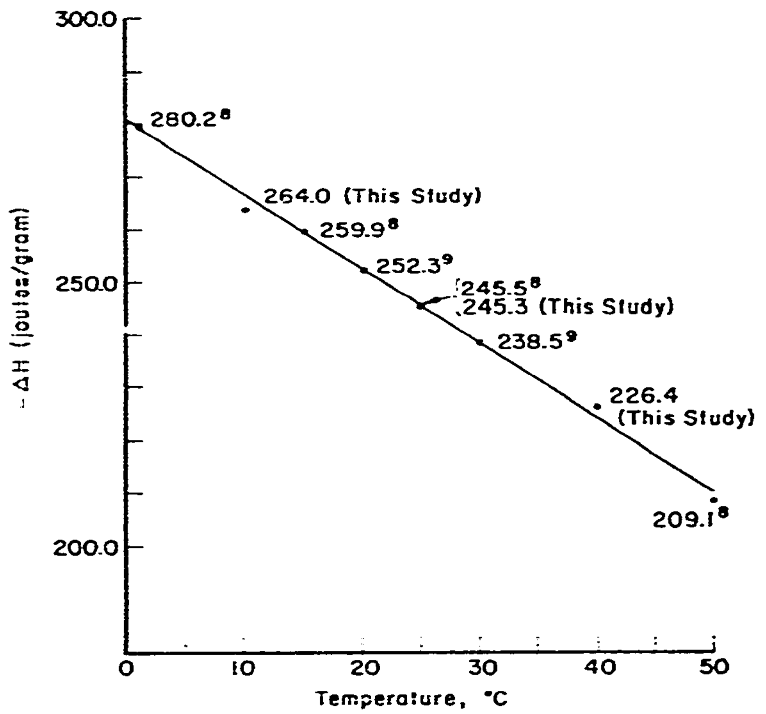

Fig. 1. Plot of heat of reaction of THAM(s) in 0.1 M HCl solutions versus temperature.

uncertainty interval for each of the values reported in this study is given as twice the standard deviation of the mean $2\sqrt{\sum(d^2)/n(n-1)}$. Figure 1 is a plot of temperature versus the ΔH value for the reaction of THAM(s) with HCl obtained in this study and that of Hill *et al.*[8] and Irving and Wadso[9], the only other authors who studied the reaction as a function of temperature.

DISCUSSION

As indicated earlier, some determinations were made with ampoules that had been carefully sealed with a flame. It was found in these cases that not only did the reaction proceed more slowly but the total heat evolved was consistently about 3% less than for those ampoules which had been sealed with Parafilm. The lower result probably resulted from partial decomposition of the THAM due to the heat of the flame. It is apparent that this method of sealing the glass ampoules is not desirable.

Ampoules sealed at 25 °C at a relative humidity of 44% (the relative humidity of this laboratory) contain about 10^{-5} g/ml of water vapor, a small portion of which may condense at 10 °C on the inside of the ampoule and on the THAM. This could prematurely dissolve some of the THAM (solubility of THAM in w[illegible] is ~0.55 g/ml at 25 °C), and, since the heat of solution is endothermic, would cause the heat of reaction to appear higher than it should be. However, the amount of condensate was calculated to be no more than 8.5×10^{-6} g for an ampoule having 14 ml free vapor space. Assuming the condensate to be entirely on the THAM, about 5×10^{-6} g of THAM would dissolve. This would be an insignificant amount. If necessary, this problem could be circumvented by filling the ampoules with nitrogen. This would be unnecessary, however, for the suggested standard temperature of 25°C.

The results of this study confirm the earlier observation that THAM would be very useful as an interlaboratory comparison standard, and it appears from the reported values in Table IV that 7.110 ± 0.003 kcal/mole (245.6 ± 0.1 joules/g) is probably the "best" value for the heat of reaction at 25°C of THAM(s) with 0.1 *M* HCl solution.

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