A Preliminary Note on Heat of Combustion of Solid Poly(vinyl alcohol) and Heat of The (Hypothetical) Polymerization of Acetaldehyde into Poly(vinyl alcohol)

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Acetaldehyde is known to polymerize into polyacetal.¹⁾ It might also polymerize into poly(vinyl alcohol) (PVA) by hypothetical reactions such as successive aldol condensations or an addition polymerization of enol. There have been some attempts on this line, but the synthesis has not yet been successful.²⁾

In the present paper, we investigated thermochemically the possibility of the formation of PVA from acetaldehyde.

A commercial sample of PVA (DP=1500) was purified by re-hydrolysis with 0.02 N alcoholic sodium hydroxide followed by dialysis. The polymer powder was dried overnight in a high vacuum manipulation, was made into tablets, and was stored in a vacuum desiccator.

The calorimetry apparatus was an isothermal jacket type bomb calorimeter, incorporating a 271 m*l* stainless steel-made bomb and Beckmann thermometers. The temperatures in the calorimeter vessel and the water jacket were observed with an accuracy of 0.001°C. The combustion measurements were carried out under 35 atm pressure of oxygen, using a platinum wire and a cotton string. For the complete burning of PVA about 0.01 g of liquid paraffin was used as a promoter (the heat of combustion of liquid paraffin= 10868 cal/g).³⁾ The calibration experiments of the calorimeter were carried out at a temperature of 25°C using benzoic acid (39h) supplied from National Bureau of Standards, Washington, D. C., and its energy equivalent value was determined to be 2518 cal/°C. The completeness of combustion was ascertained by visual inspection of the bomb contents for traces of black materials.

The results of six combustion experiments are given in Table 1, in which the energy evolved per monomeric unit at 25°C is represented by $-\Delta U_B$,

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1) J. Furukawa and T. Saegusa, "Polymerization of Acetaldehyde and Oxides," John Wiley & Sons., New York (1963).

2) *Ibid.*, p. 109.

3) T. Tanaka, U. Takahashi, R. Okawara and T. Watase, This Bulletin, **28**, 15 (1955).

Table 1. The experimental data for poly(vinyl alcohol) at 25°C

Wt. of sample g	Total heat evolved cal	$\sum$ cal	$\sum'$ cal	$-\Delta U_B$ kcal. per monomer unit
0.7108	6100.3	3.2	128.9	262.9
0.7056	6157.5	1.6	175.0	263.5
0.7119	6078.8	1.5	131.2	262.0
0.7151	6126.6	2.5	127.3	264.2
0.7022	6117.1	2.6	150.5	262.7
0.7138	6096.5	2.3	125.9	262.9
				mean 263.0 ± 0.5

$\sum$ is the calorific value from nitric acid, and $\sum'$ is the sum of the heat of combustion of the promoter and the cotton string. The value of the bomb process was then corrected to the standard constant-volume process by means of Washburn's equation.[4] The energy $(-\Delta U°_C)$ evolved in this process was 262.8 kcal/monomer unit. From this quantity the heat evolved in the isobaric process at 1 atm $(-\Delta H°_c)$ was obtained by the addition of the proper work term. The value of $-\Delta H°_c$ was 263.2 kcal/monomer unit.

The heat of combustion $(-\Delta H°_c)$ of liquid acetaldehyde is known to be 278.6 kcal/mol.[5] And hence, the heat of polymerization of acetaldehyde into partially crystalline PVA in the present case is -15.4 kcal/monomer unit.

Recently the heat of fusion of PVA (ΔH_m) was determined to be 1.64 kcal/monomer unit by the diluent method using differential thermal analysis.[6] The crystallinity of PVA used in this experiment was about 0.29.[7] Accordingly the polymerization of liquid acetaldehyde into amorphous PVA is an exothermic reaction as much as -14.9 kcal/monomer unit.

It is interesting that the magnitude of the heat of the (hypothetical) polymerization of acetaldehyde into PVA is comparable to that of the usual vinyl polymerization (-15—-25 kcal/monomer unit).[8]

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[4] E. W. Washburn, *Bur. Standards J. Research,* **10,** 525 (1933).

[5] M. S. Kharasch, *ibid.,* **2,** 359 (1929).

[6] R. K. Tubbs, *J. Polymer Sci.,* **A3,** 4181 (1965).

[7] H. Tadokoro, S. Seki and I. Nitta, This Bulletin, **28,** 559 (1955).

[8] F. S. Dainton, "Experimental Thermochemistry", **2,** Chapter 12, ed. by H. A. Skinner, Interscience Pub., New York (1962).