Heat of Reaction between Hydrogen Peroxide and Hydriodic Acid in Aqueous Solution

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HYDROGEN PEROXIDE reacts with excess hydriodic acid in an exothermic manner according to the equation

$$H_2O_2 + 3HI \rightarrow I_3^- + H^+ + 2H_2O$$

The stoichiometry of this reaction is well established and forms a basis for the quantitative determination of hydrogen peroxide (*2*).

The present investigation was undertaken to determine the experimental heat of reaction.

EXPERIMENTAL

Calorimeter. The calorimeter consists of a 660-ml. vacuum flask and a wood cover with cork gaskets. Passing through the cover are separate glass-enclosed electrical leads to a heater and a thermistor, an off-center stirrer shaft driven by a constant speed motor, and an ampoule-crushing device. The crushing device, a glass plunger with a bell-shaped serrated edge, initiates the reaction by breaking a thin soft glass ampoule containing aqueous hydrogen peroxide.

Temperature changes are recorded on a Sargent-SR potentiometric recorder, utilizing a Wheatstone bridge network. The bridge consists of two fixed resistances of 100 and 1 kilohm, a variable 1-kilohm resistance, and a thermistor (Victory Engineering 51A11, 100-kilohm). It is powered by three 1.3-volt mercury batteries in series. The out of balance potential is a linear function of the temperature difference. After the thermistor had been annealed at 100° C. for 2 weeks, the temperature-measuring apparatus was found to be reproducible over an extended period. It was calibrated against an NBS-certified mercury-in-glass thermometer.

A heater of 108.4 ohms of coiled Manganin wire immersed in Octoil and contained in a glass U-shaped tube is used to determine the energy equivalent of the calorimeter after each run. Leads to the heater are of No. 24 copper wire. The energy for the heater is supplied by lead storage batteries that are discharged into a dummy resistor for 1 hour to stabilize the voltage. The heater current is determined from the potential drop across a standard 1-ohm resistance in series with the heater, measured with a Leeds & Northrup Type 8691 potentiometer. The time of heating is given by an electric stopclock synchronized with the heater switch.

The calorimeter is enclosed in an air thermostat regulated by a Tri-R Instruments thermistor controller at 26.7° ± 0.1° C.

Reactions were carried out under conditions of excess hydriodic acid. In a run 200 to 250 ml. of 0.3 to 0.4*N* HI were placed in the Dewar. After the ampoule containing the H_2O_2 had been broken, the reaction went to completion in less than 5 minutes. Corrections for heat exchange were carried out (*6*). These were in all cases very small.

Materials. Hydriodic acid was prepared by adding water dropwise to a mixture of red phosphorus and iodine (*5*). The liberated gaseous HI passed through a trap filled with red phosphorus and bubbled into rapidly stirred distilled water.

Prior to use, the aqueous HI was purified by distillation and determined by precipitation at pH 5 with standard $AgNO_3$ and eosin indicator.

H_2O_2 solutions were prepared by dilution of reagent grade 30% H_2O_2. Weighed samples were determined prior to each run with standard $KMnO_4$ or with excess HI, followed by titration of the liberated iodine with standard thiosulfate. Both methods yielded identical results.

RESULTS AND DISCUSSION

Applying heat of dilution corrections (*1, 4*) to the average ΔH_r from Table I, we obtain for

$$H_2O_2(aq) + 3HI(aq) \rightarrow 2H_2O(l) + H^+ + I_3^-(aq)$$

$\Delta H_r^0 = -63.3$ kcal. per mole, with an estimated experimental error of 2.0 kcal. per mole. This result is in excellent agreement with that derived from heats of formation of the infinitely dilute species listed in the NBS tables, $\Delta H_r^0 = -63.3$ kcal. per mole. The latter heat, however, is subject to an error greater than 1 kcal. due to the uncertainty that exists in the value (*3*) for ΔH_f^0 of I_3^-.

Table I. Heats of Reaction of HI and H_2O_2 in Aqueous Solution

H_2O_2, Mole $\times 10^2$	H_2O_2, *N* $\times 10^2$	HI, Moles $\times 10^2$	HI, *N* $\times 10^2$	Corrected ΔT^a	Total Energy Change, Cal.	$-\Delta H_r$, Kcal. /Mole H_2O_2
0.655	5.24	7.58	30.3	1.52	400	61.2
0.686	5.49	8.15	32.6	1.62	452	65.8
0.383	3.83	6.12	30.6	1.10	243	63.4
0.523	5.23	6.64	33.2	1.56	347	66.3
0.419	4.19	6.38	31.9	1.22	265	63.2
0.892	6.62	10.80	40.0	1.97	570	63.9
0.647	6.47	7.50	37.5	1.97	419	64.8
0.614	6.14	7.14	35.7	1.80	378	61.7

Av. $\Delta H_r = -63.8$ kcal./mole.
Av. dev. = 1.4 kcal./mole.
^{a} (± 0.003° C.)

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