

477. *The Thermochemistry and Pyrolysis of Bishydroxymethyl Peroxide.*

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The heats of formation of bishydroxymethyl peroxide in the solid and in the gaseous state and in aqueous solution have been determined. The decomposition of the vapour has been investigated at low pressures and at temperatures between 100° and 200°. The products are explicable in terms of two modes of decomposition, one yielding formaldehyde and the hydroperoxide, and the other hydrogen and formic acid. As the temperature was raised, the hydroperoxide became increasingly unstable and could not be isolated above 200°.

ALTHOUGH bishydroxymethyl peroxide is frequently found among the products of the reaction of a number of simple organic molecules with oxygen, very little is known about the properties of its vapour. As normally prepared, this substance contains about 1% of impurities, which appear to be mainly inclusions of solvent and perhaps of polymeric formaldehyde and hydrogen peroxide. The removal of the last traces of these impurities is difficult and hazardous, since the peroxide may explode violently if heated too strongly, and prolonged exposure to vacuum, especially in the presence of phosphoric oxide, can produce a product which approaches nitrogen iodide in sensitivity. A somewhat impure material has consequently been used for the investigation of the thermochemistry and thermal decomposition of the peroxide, and no great precision is claimed for the measurements. The final thermochemical results may be in error by 4 or 5 kcal.

EXPERIMENTAL

Preparation and Estimation of Peroxide.—Bishydroxymethyl peroxide was prepared by vacuum-concentration over concentrated sulphuric acid of a mixture of 35% aqueous formaldehyde (2 mols.) with 30% aqueous hydrogen peroxide (1 mol.). The thick syrup first obtained gradually crystallised. The crystals were filtered off and twice recrystallised from freshly redistilled ether, the ethereal solution being dried (Na_2SO_4). The product was 98–99% pure according to the volume of hydrogen evolved when it was treated with excess of concentrated sodium hydroxide solution, and *ca.* 98% by titration with ceric sulphate. Since ceric sulphate does not react with the peroxide but only with its hydrolysis product, H_2O_2 (Dunicz, Perrin, and Style, *Trans. Faraday Soc.*, 1951, **47**, 1210), this determination was carried out by adding an excess of standard ceric sulphate solution to a known weight of peroxide, making the solution strongly acid with concentrated sulphuric acid, and heating the solution to 70° for 10 minutes, whereby complete hydrolysis to hydrogen peroxide, which immediately reacted with ceric sulphate, was accomplished. After the solution had cooled to room temperature, the excess of ceric sulphate was back-titrated with standard hydrogen peroxide solution.

Thermochemical Measurements.—Latent heat of sublimation. This was obtained from the temperature dependence of the vapour pressure, which was measured by a dynamic method. B.D.H. "Extra pure" benzene for molecular-weight determinations, which was found to be quite inert toward the peroxide, was used as the carrier gas. The benzene vapour at a constant pressure of 20 mm. Hg was passed slowly through a 100-cm. length of tubing of 5-mm. bore loosely packed with crystalline peroxide, the time of contact being about 10 sec. Following this saturator and in the same thermostat was a length of capillary tubing, across which the gas pressure fell sufficiently to prevent condensation of peroxide vapour in the subsequent tubing exposed to the atmosphere which led to the trap cooled in solid carbon dioxide-alcohol in which all the benzene and peroxide were frozen out. The system was evacuated with a "Hyvac" oil-pump. At the end of an experiment, which lasted 2–6 hours, the trap containing the condensate was removed, stoppered, warmed to room temperature, and weighed. The peroxide content was titrated with ceric sulphate as described above, and after being washed and dried, the empty trap was again weighed. The vapour pressure of the peroxide was calculated from these data, it being assumed that both vapours behaved as perfect gases and were unassociated. Reduction of the rate of flow to about half the usual value did not alter the calculated vapour pressure.

The smallness of the vapour pressure below 15° , and evidence of decomposition of the solid peroxide above 40° , limited the usable temperature range. The results are given below. The values for 15° are rather high, but the others are well represented by $\log p = 15.423 - 4910/T$, corresponding to a latent heat of sublimation of $22.5 \text{ kcal. mole}^{-1}$ ($94.2 \text{ kJ mole}^{-1}$).

<i>T</i>	15.0°	20.1°	25.0°	30.0°	34.8°	39.3°
<i>p</i> , mm.	0.039, 0.034	0.049	0.070	0.167, 0.160	0.302	0.524

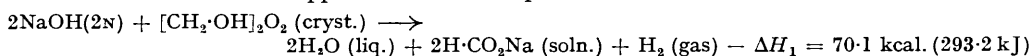
Heat of solution. The heat of solution of the peroxide in water was determined calorimetrically. The calorimeter, a Dewar flask of about 500-ml. capacity, was supported in a thermostat kept at 25° . The top of the flask was closed by a cork stopper through tubes inserted into which passed the small electrically-operated stirrer, a Beckmann thermometer used as an indicating instrument, and the leads to the heating coil by means of which the heat capacity of the calorimeter and its contents was calibrated. The heat absorbed when one mole of peroxide was dissolved was independent of the final concentration over the range investigated, as shown by the following data. The average value of the heat of solution, $-\Delta H_s$, at 25° is $5.25 \text{ kcal. mole}^{-1}$ ($22.0 \text{ kJ mole}^{-1}$).

Final molarity	0.0435	0.0556	0.0943	0.1428	0.1652
$-\Delta H_s$, kcal. mole $^{-1}$	5.22	5.41	5.21	5.16	5.25

Heat of reaction $[\text{CH}_2\text{OH}]_2\text{O}_2 + 2\text{NaOH} \longrightarrow 2\text{H}_2 + 2\text{H}\cdot\text{CO}_2\text{Na}$. The decomposition of the peroxide is strongly catalysed by hydroxyl ion and in the presence of 2*N*-sodium hydroxide it is very rapid, as is also the rate of solution of the solid peroxide. The heat evolved ($-\Delta H_1$) when various amounts of solid peroxide were added to 100 ml. of 2*N*-alkali solution are collected below. The average of the last four is $-\Delta H_1 = 69.8 \text{ kcal. mole}^{-1}$ ($292.0 \text{ kJ mole}^{-1}$).

Peroxide, m.-moles	0.553	1.085	1.819	2.149	2.298
$-\Delta H_1$, kcal. mole $^{-1}$	62.5	69.1	69.7	71.6	68.9

The formation of gaseous hydrogen introduces an uncertainty, for were all the hydrogen to remain in solution a correction for this heat of solution, estimated at +0.6 kcal. (from the variation of solubility with temperature, Landolt-Börnstein, "Tabellen," 5th Edn., p. 763), would be necessary, whereas if all the hydrogen escapes saturated with water vapour the corresponding latent heat correction is -0.3 kcal. There was, in fact, a brisk evolution of hydrogen and the correction will be applied on the assumption that none remained in solution:



The heat of formation of the crystalline peroxide from its elements ($-\Delta H_f$) may be obtained from ΔH_1 with the aid of Bichowski and Rossini's data ("Thermochemistry of Pure Substances," Reinhold, New York, 1936) for the heat of formation of sodium formate in dilute aqueous solution, $-\Delta H_2 = 157.3 \text{ kcal. mole}^{-1}$, the heat of formation and the differential heat of solution of crystalline sodium hydroxide, $\Delta H_3 = 102.0 + 10.5 = 112.5 \text{ kcal.}$, and the heat of formation and differential heat of solution of liquid water $\Delta H_4 = 68.4 + 0 = 68.4 \text{ kcal.}$ The heats of formation apply to 291° K. Rough estimates indicate that the use of these in conjunction with ΔH_1 obtained at 298° K. will not introduce any error exceeding the experimental uncertainty. We then have,

$$\begin{aligned} \Delta H_f, [\text{CH}_2\cdot\text{OH}]_2\text{O}_2 (\text{cryst.}) &= 2\Delta H_2 + 2\Delta H_4 - \Delta H_1 - 2\Delta H_3 \\ &= -156.3 \text{ kcal. mole}^{-1} (653.8 \text{ kJ mole}^{-1}) \end{aligned}$$

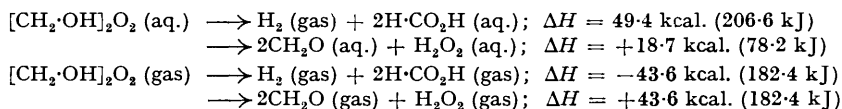
and from the heat of solution and latent heat of sublimation (all in kcal. mole⁻¹)

$$\Delta H_f, [\text{CH}_2\cdot\text{OH}]_2\text{O}_2 (\text{gas}) = -133.8; \Delta H_f, [\text{CH}_2\cdot\text{OH}]_2\text{O}_2 (\text{aq. soln.}) = -151.0$$

With the additional heats of formation (Bichowski and Rossini, *op. cit.*)

$$\begin{aligned} \Delta H_f, \text{H}\cdot\text{CO}_2\text{H} (\text{gas}) &= -88.7; \Delta H_f (\text{CH}_2\text{O}, \text{gas}) = -28.3; \Delta H_f (\text{CH}_2\text{O}, \text{aq.}) = -43.3 \\ \Delta H_f, \text{H}\cdot\text{CO}_2\text{H} (\text{aq.}) &= -100.2; \Delta H_f (\text{H}_2\text{O}_2, \text{gas}) = -33.6; \Delta H_f (\text{H}_2\text{O}_2, \text{aq.}) = -45.7 \end{aligned}$$

we obtain

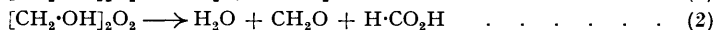
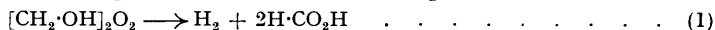


Products of Thermal Decomposition.—This was intended to be preliminary to a more complete investigation which, however, proved to be impracticable. The peroxide vapour was sublimed from a bulb containing a few g. of solid peroxide, kept at 45°, through a heated tap which slightly restricted the flow and reduced back-diffusion of the decomposition products formed in the immediately following cylindrical reaction chamber of diameter 4 cm. and volume *ca.* 200 ml. Leaving the reaction chamber, the products of decomposition passed through a length of narrow-bore tubing and a tap into two traps, the first to remove undecomposed peroxide (only observed below 150°) and the second cooled in liquid air to remove all products other than hydrogen and carbon monoxide, which were collected by a Töpler pump and transferred to the conventional gas-analysis apparatus. The peroxide reservoir and the reaction chamber were heated by manually controlled oil-baths. Preliminary examination of the condensable products showed the presence of formaldehyde (smell), water (restoration of blue colour to dehydrated copper sulphate), acid, and at lower temperatures hydroperoxide (immediate reaction with acid ceric sulphate solution). In the early experiments oxygen was found among the gaseous products. The amount decreased with time and ultimately became zero. It probably arose from hydrogen peroxide impurity in the organic peroxide. The absence of oxygen in the permanent gases from acceptable experiments indicates that the peroxide present in the condensable products is not hydrogen peroxide. This is confirmed by element balances which are best satisfied if the peroxide is $\text{CH}_2(\text{OH})\cdot\text{O}\cdot\text{OH}$ (hydroxymethyl hydroperoxide), which in low concentration is titratable by ceric sulphate (Dunicz, Perrin, and Style, *loc. cit.*).

It was not practicable to attempt quantitative analysis for all these substances in the products collected from any one run. Each of the above condensable products, other than water, was estimated one at a time in separate runs together with the corresponding amount of hydrogen and carbon monoxide. The results of the individual estimations could then be brought to a common basis—a standard amount of hydrogen.

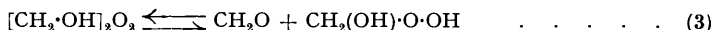
Formaldehyde was estimated colorimetrically with chromotropic acid (Bricker and Johnson, *Ind. Eng. Chem. Anal.*, 1945, **17**, 400). The first trap was cooled with ice-salt and retained the organic peroxides which would otherwise have been hydrolysed to additional formaldehyde during the estimation. Formic acid was estimated by titration with 0.02N-sodium hydroxide

to pH 7. Peroxide was estimated by titration with ceric sulphate in strongly acid solution. The variation with temperature of the molar proportions of the various products scaled to one mole of hydrogen is shown in Fig. 1. At the highest temperature, peroxide formation was negligible and the proportions of the products were those to be expected from

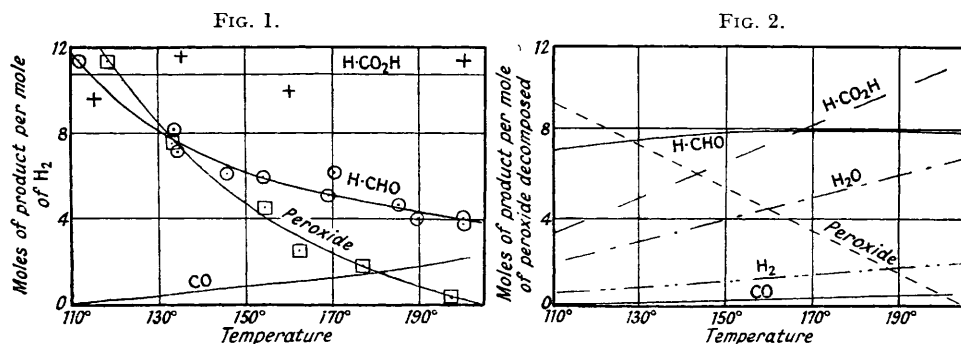


together with a small amount of decomposition of formic acid into water and carbon monoxide.

The appearance of increasing amounts of peroxide as the temperature is reduced required a third decomposition process. The reaction (3) is consistent with the observations at tem-



peratures above 150°. Below this temperature there is obviously a small discrepancy in the analysis, there being either too little formaldehyde or too much hydroperoxide. Since it only occurs when some of the initial peroxide remains undecomposed, the discrepancy probably arises from the partial titration of undecomposed bishydroxymethyl peroxide which would give too large amounts of peroxidic products. An estimated correction, varying from zero at 150° to 10% at 120°, has been applied to the amount of hydroperoxide found before deriving



the data upon which are based the curves of Fig. 2, which shows how the products from one mole of bishydroxymethyl peroxide vary with the temperature.

Whereas bishydroxymethyl peroxide loses one formaldehyde molecule fairly easily, indeed more readily than it breaks down into hydrogen and formic acid, the loss of the second molecule of formaldehyde by hydroxymethyl hydroperoxide appears to occur to a negligible extent compared with the decomposition into water and formic acid. The heat of formation of gaseous bishydroxymethyl peroxide from gaseous formaldehyde and hydrogen peroxide [$\Delta H = -43.6$ kcal. mole⁻¹ (182.4 kJ mole⁻¹)] is so large that the reverse dissociation would scarcely have been expected. It is regrettable that there is no easy means of obtaining ΔS of this reaction, and hence its equilibrium constant. Evidence for the formation of bishydroxymethyl peroxide in this way is perhaps to be found in the presence of bishydroxymethyl peroxide among the products of the oxidation of gaseous formaldehyde at *ca.* 300° (Bone and Gardner, *Proc. Roy. Soc.*, 1936, *A*, **154**, 297) and of the (heterogeneous?) reaction in a Pyrex vessel at 100° (E. C. A. Horner, unpublished). Reaction (3) is thus probably a reversible reaction, which may well be very largely repressed in the presence of a large excess of formaldehyde such as would be present in most investigations of its oxidation. Since reaction (2) presumably represents the final result of (3), followed by decomposition of the hydroperoxide into water and formic acid, decomposition of bishydroxymethyl peroxide in the presence of excess of formaldehyde should be relatively slow and proceed very largely according to reaction (1), with a ratio of formic acid to hydrogen in the products of 2 : 1, or a little greater if reaction (3) is not completely suppressed. Ratios of this magnitude have been obtained by Summers at 200° and 250° [$(\text{H}\cdot\text{CO}_2\text{H})/(\text{H}_2) = 2.7$ and 2.2 , respectively] (Summers and Style, *Trans. Faraday Soc.*, 1946, **42**, 388) in the photochemical oxidation of formaldehyde. Similar values have also been obtained by E. C. A. Horner from the same reaction.

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