contained a water–ice mixture. The whole apparatus was shaken in a steady up and down motion, and the temperature was observed to decrease slowly to 0°. Neither pure nitrobenzene nor the solutions of the addition compounds froze at this temperature as they had a great tendency to supercool. To induce freezing, the cell was removed from the Dewar, and a piece of Dry Ice was touched to the outside of the cell. Freezing was observed immediately, the cell was returned to the Dewar, shaken well and the temperature was recorded every thirty seconds.

To determine the melting points, the ice-water in the Dewar flask was replaced with water at a temperature of about 8°. The cell containing the frozen nitrobenzene or solution was placed in the Dewar and the temperature of the system read every 30 seconds as the solid melted. With pure solvent the temperature remained constant for a long period of time, and then increased rapidly when the solid had melted. The freezing and melting temperatures for the purified nitrobenzene agreed to within 0.005°. Apparently, the method of mixing and the procedure in general were satisfactory.

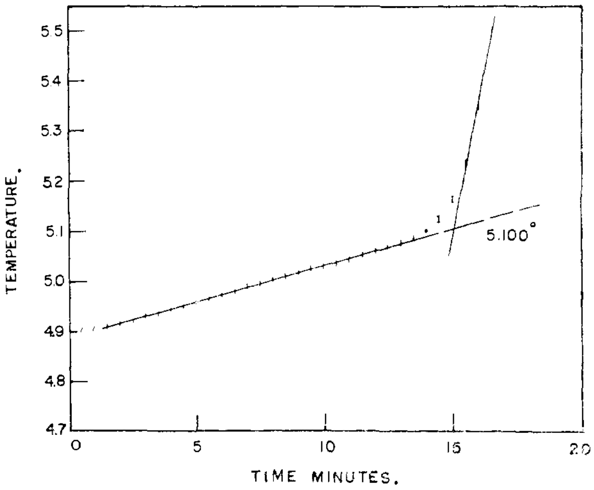

Fig. 1.—Typical melting curve—$HfCl_4 \cdot 2POCl_3$ in nitrobenzene.

When a solute was dissolved in the nitrobenzene, both the freezing and the melting curves were determined. In either case however the true freezing point of the solution had to be determined by extrapolation to zero time, the time of initial freezing, in order to correct for the change in freezing point as the concentration of the solution changed with the amount of solvent crystallized out. It was concluded that the true freezing point of the solutions could be best determined from the melting point curves, since the extrapolation was shorter and more precisely made (Fig. 1).

Procedure of X-Ray Diffraction Samples.—A Debye–Scherrer type powder camera was used which had a diameter of 114.59 mm. The radiation used was Cu $K\alpha_{1,2}$ with a Ni filter. The tube was run at 37 kilovolts and 20 milliamp. Exposures of 8–9 hours were required. The lines obtained with these samples were rather broad, and it was difficult to locate the centers to an accuracy of better than 0.1 mm. The maximum error in θ would be then 6′ of a degree.

The tetrachloride patterns were taken on freshly sublimed samples contained in a Pyrex capillary. The addition compound specimens were prepared in the following manner. In a dry box, an aliquot of a saturated solution of the metal tetrachloride in phosphorus oxychloride was transferred by means of a capillary eye dropper into thin-walled capillary tubes bent in the shape of a U. It was necessary to have the liquid in the tubes unbroken by air bubbles. The filled capillaries were transferred to a container which was then attached to a vacuum manifold. The excess phosphorus oxychloride was removed under 30 mm. pressure of dry air at room temperature to leave a deposit of $MCl_4{:}2POCl_3$. The $MCl_4{:}POCl_3$ specimens were prepared by heating the vessel containing the capillaries *in vacuo* at 110° for eight hours. The final trace of solvent was removed by pumping on the system directly. The portion of the capillary tube which contained a heavy solid deposit was cut into one inch lengths and sealed with beeswax.

MADISON, WISCONSIN

NOTES

Peroxide Yield in the γ-Irradiation of Air-saturated Water[1]

BY AUGUSTINE O. ALLEN AND RICHARD A. HOLROYD

RECEIVED JUNE 30, 1955

The formation of peroxide in air-saturated water, irradiated with X- or γ-rays, is one of the oldest and most frequently studied reactions in radiation chemistry. The first detailed study of this reaction was made by Risse[2] in 1929. A careful study was published by Fricke[3] in 1935, and many more studies have appeared.[4] The rate of peroxide formation is found in general to decrease as the peroxide accumulates and eventually to become zero as the peroxide reaches a steady-state level. Published values of the initial yield range from 1.1 to 2.0. This yield is of interest in connection with studies of the mechanism of water decomposition under irradiation.[5] Discrepancies in the reported initial yields occur in part because of ambiguity in the interpretation of what is meant by initial values. Some of the data, particularly of Hochanadel[4a] and of Hart and co-workers,[4b] appear to indicate a very short initial period of relatively rapid peroxide formation extending up to no more than a very few μmoles per liter of peroxide, followed by a longer period at a nearly constant rate extending up to 30–100 μ*M* with gradually decreasing rate at higher concentrations. Hochanadel and others have regarded the constant rate appearing after the short initial portion as being the correct yield, or have ignored the existence of the very short initial period, but Hart and co-workers have regarded the higher figure of the initial period as the true yield.

Sworski[4c] recently has shown that the peroxide yield decreases on the addition of bromide ion at *p*H

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(1) Research performed under the auspices of the U. S. Atomic Energy Commission.

(2) O. Risse, *Z. physik. Chem.*, **A140**, 133 (1929).

(3) H. Fricke, *J. Chem. Phys.*, **3**, 556 (1935).

(4) (a) C. J. Hochanadel, *J. Phys. Chem.*, **56**, 587 (1952); (b) E. J. Hart, S. Gordon and D. A. Hutchison, Abstracts, American Chemical Society Meeting, Los Angeles, March, 1953; (c) T. J. Sworski, THIS JOURNAL, **76**, 4687 (1954); (d) T. Alper, M. Ebert, L. H. Gray, M. Lefort, H. C. Sutton and F. S. Dainton, *Discs. Faraday Soc.*, **12**, 206 (1952).

(5) A. O. Allen, *Radiation Research*, **1**, 85 (1954).

2 to the water. The decrease is of particular interest in current attempts to interpret the mechanism of water decomposition by radiation. It seemed especially timely therefore to attempt to establish just what value of the rate should be regarded as representing the theoretically significant initial yield and to confirm and extend Sworski's observations of the effect of bromide ion upon this quantity.

Experimental

Purification of the water used is very critical as far as results on peroxide yields are concerned. Redistilled water is prepared in this Laboratory by a continuous system. Distilled water from the laboratory supply is fed continuously into a boiling flask containing acid dichromate. Vapors from this solution are condensed and fall into a second boiling flask containing alkaline permanganate. A third flask follows for a final distillation.

In order to purify this water further we used the suggestion of Fricke[6] that the best purification reagent for an irradiation study should be radiation itself. Samples of air-saturated redistilled water were irradiated for several hours in the Co^{60} source until a concentration of some hundreds of μmoles per liter of peroxide had been built up. The water was then poured into a carefully cleaned and steamed-out tube of fused silica and photolyzed by placing it inside the coil of a helical Hanovia SC-2537 low pressure mercury resonance lamp run at 50 ma. from a 6000 volt transformer. Two-hours of photolysis was sufficient to destroy all the peroxide. The photolyzed sample was surrounded by a filter consisting of a solution of KI (0.155 g./l.) and I_2 (0.108 g./l.) to cut out the far ultraviolet. Without this filter the 1849 Å. component built up small concentrations (3–4 μM) of peroxide in air-saturated water, and peroxide in solution could not be completely destroyed. From the photolysis container the water was poured into a carefully cleaned and steamed-out flask for storage.

Irradiations were made in a Co^{60} source described elsewhere.[7] Sample tubes were always pre-irradiated to a pronounced brown color before use, were thoroughly steamed out, and kept filled with purified water. Yield values were calculated by comparison with the yield of oxidation of ferrous sulfate, the absolute yield for the dosimeter being assumed as $G = 15.5$.

Results

At the start of this study, pure air-saturated water from the still gave peroxide-dose curves on irradiation like those shown as the upper curve in Fig. 1. The initial rapid build-up extended to concentrations of about 10 μmoles per liter, before the rate fell off to a lower value. The question was whether the initial rapid period was due to the effect of impurities in the sample or was really characteristic of pure water. In an attempt to improve the purity of the water, the redistillation apparatus was completely disassembled, cleaned and reassembled in a design which incorporated two improvements over the previous design: (a) distilled water was introduced entirely through glass tubing, not being allowed to touch any plastic or rubber tubing in the course of its passage into the apparatus; (b) the connection of the take-off part of the apparatus with the atmosphere, necessary in order to equalize pressure, was made through a train containing silica gel and activated charcoal. With this improvement the peroxide formation was given by the middle curve in Fig. 1. Here the initial rapid build-up is confined to about the first 2 μmoles per liter of peroxide to be formed. The lowest curve in Fig. 1 is a combination of three runs obtained on water samples which had been purified by the radiolysis–photolysis procedure described above. Here a straight line is found having only a very small intercept, indicating an extremely small initial period of rapid build-up. A similar curve with a small intercept is shown by Hochanadel.[4a]

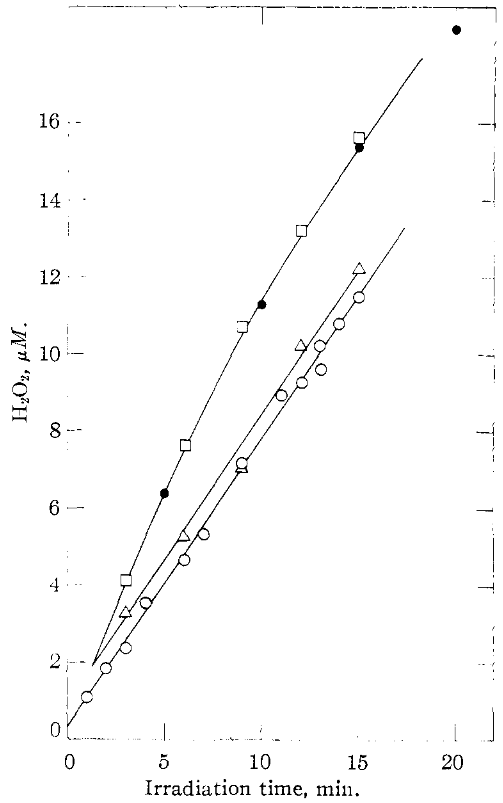

Fig. 1.—Formation of peroxide by γ-rays in air-saturated water: ●, triple-distilled water; □, the same with an additional distillation from alkaline $KMnO_4$; △, triple-distilled water after still was cleaned and modified; ○, treated by radiolysis + photolysis. Source intensity, 9.6 μM $FeSO_4$ oxidized per min.

It is reasonable to conclude that the initial high rate results from the existence of impurities which are soon consumed in the reaction, and that the true rate corresponding to pure air-saturated water is given by the slope of the curve after the initial portion is passed through. That organic substances may increase the yield of peroxide in irradiated air-saturated water was shown years ago by Loiseleur and Latarjet.[8] The reason for this effect is easy to see on the free radical theory. Hydroxyl radicals act to destroy peroxide (which is built up by the action of hydrogen atoms on dissolved oxygen) and anything which offers an alternative reaction for the free OH radicals should tend to increase the observed yield of peroxide. The effect of impurities on the peroxide yield is apparently greater than their effect on the oxidation of ferrous sulfate. The magnitude of the intercept found in curves like those in Fig. 1 is an extremely sensitive test for the amount of organic matter contained in a sample of

(6) H. Fricke, E. J. Hart and H. P. Smith, *J. Chem. Phys.*, **6**, 229 (1938).

(7) H. A. Schwarz and A. O. Allen, *Nucleonics*, **12**, No. 2, 58 (1954).

(8) J. Loiseleur, R. Latarjet and C. Crovisier, *Compt. rend. soc. biol.*, **136**, 57 (1942).

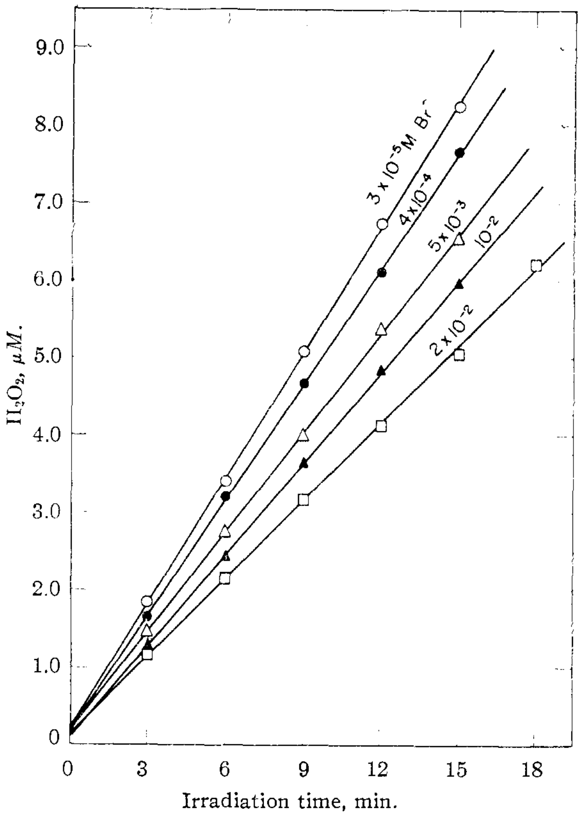

Fig. 2.—Formation of peroxide by γ-rays in air-saturated neutral bromide solutions.

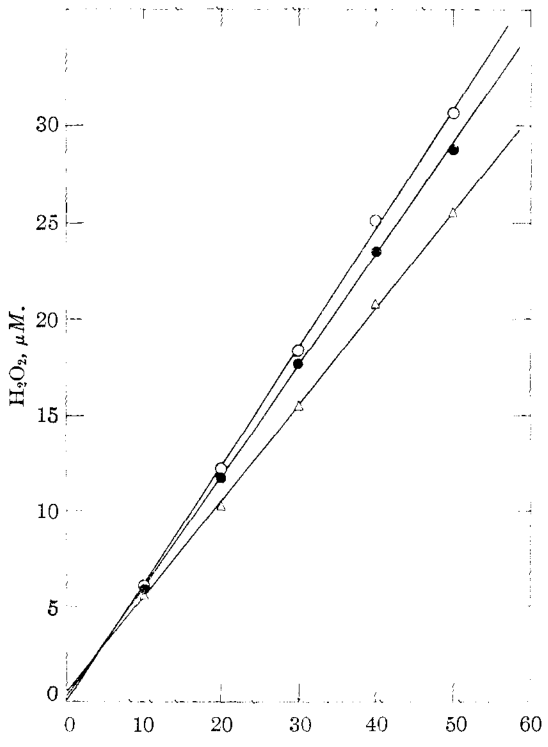

Fig. 3.—Formation of peroxide by γ-rays in air-saturated 0.01 N H_2SO_4 containing KBr: ○, 10^{-4} M Br^-; ●, 5 × 10^{-4} M; △, 5 × 10^{-3} M.

water. From the slope of the curves in Fig. 1 we find $G_{H_2O_2} = 1.23$ for pure water in equilibrium with ordinary air (*p*H ~5). Results on bromide solutions are shown in Figs. 2 and 3 and the *G* values are assembled in Fig. 4. All the results in neutral bromide solutions were obtained using water prepared by the radiolysis–photolysis method. The acid bromide results were obtained with redistilled water. Intercepts are seen to increase somewhat with addition of bromide to the solution, probably owing to some impurity associated with preparation of the solutions.

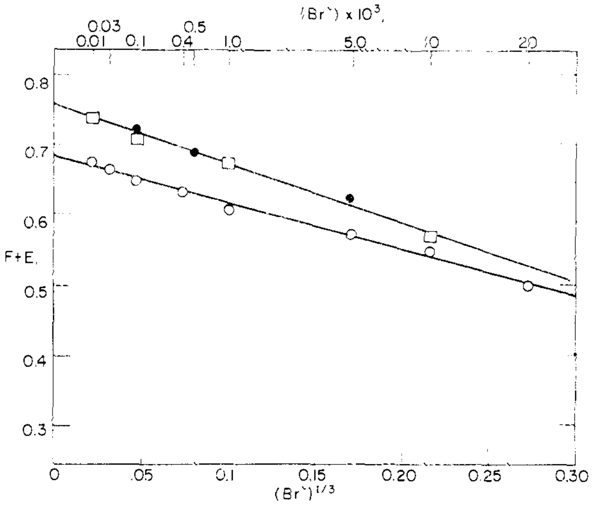

Fig. 4.—Molecular peroxide yield from γ-rays in water as a function of Br^- concentration; □, *p*H 2, data of Sworski[4c]; ●, *p*H 2, present work; ○, *p*H about 5, present work

The quantity plotted in Fig. 4 is not the observed total peroxide yield, but that part of the peroxide yield which is calculated to arise directly from water decomposition, called $F + E$. As pointed out by Allen[5] and by Sworski,[4c] if the yield of H_2 from water decomposition is F, and that of H_2O_2 is $F + E$, then an excess of H atoms over OH radicals in the amount of $2E$ must be produced, which will be available for reducing dissolved oxygen to form an additional E moles of H_2O_2, so that the total observed yield of peroxide per 100 ev. absorbed will be $F + 2E$. To calculate the molecular peroxide yield, $F + E$, from the observed yield, we must add to the observed yield the hydrogen yield, F, and divide by 2. According to Schwarz, Losee and Allen[9] the best value of F is 0.45. Accordingly the quantity plotted in Fig. 4 is $^1/_2(G_{obs} + 0.45)$, which quantity was also plotted by Sworski.

Our results at *p*H 2 are seen to be in exact agreement with Sworski. The yields with no sulfuric acid added (*p*H ~5) are lower than in the acid solutions. Empirical equations for the yield as a function of bromide concentration, from least-square calculations (including Sworski's data corrected to $F = 0.45$ and $G(Fe^{++}) = 15.5$), are: at *p*H 2, $F + E = 0.77 - 0.93\,(Br^-)^{1/3}$; in neutral solution, $F + E = 0.685 - 0.65\,(Br^-)^{1/3}$.

At bromide concentrations below 10^{-5} M results were erratic and $G_{H_2O_2}$ appeared to be higher. This

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(9) H. A. Schwarz, J. P. Losee and A. O. Allen, This Journal, 76, 4693 (1954).

was expected since, as Sworski has pointed out, when insufficient bromide is present to protect the H_2 which is formed from water decomposition, this H_2 will partly be drawn into the reaction by free OH radicals and thereby add to the yield of H_2O_2. The observed yield in pure water is therefore higher than the value found by extrapolating the yields in bromide solution to zero bromide concentration. The extrapolated values, shown as intercepts in Fig. 4, should however give the true value of $F + E$ in water. This value is seen to be higher in 0.01 N sulfuric acid than in air-saturated water by about 0.085. Increasing the H_2SO_4 concentration to 0.8 N increases $F + E$, according to Sworski, by an additional 0.03.

Schwarz[10] has derived the variation of $F + E$ with bromide concentration on the basis of a simple radical diffusion model. No explanation is evident at present for the variation of $F + E$ with acid concentration.

(10) H. A. Schwarz, This Journal, **77**, 4960 (1955).

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Thiophene: Heat of Combustion and Chemical Thermodynamic Properties[1]

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RECEIVED JULY 5, 1955

As part of a study in this Laboratory,[2] of the thermodynamic properties of thiophene the heat of combustion was determined by the Huffman–Ellis method[3] in a conventional type of bomb calorimeter. The value of the heat of formation thereby obtained was published as a preliminary value only, because it was realized that the Huffman–Ellis method for sulfur compounds was inadequate for combustion calorimetry of the accuracy desired. The preliminary datum was not deemed reliable enough for use in calculating the heat and free energy of formation of thiophene as a function of temperature. Since publication of this earlier work, a rotating-bomb method[4] has been developed for the combustion calorimetry of sulfur compounds and has been shown to give more reliable results than the Huffman–Ellis method. The heats of combustion and formation of thiophene have now been redetermined by the rotating-bomb method. This note reports the more reliable results obtained with the improved method and gives values for the heat and free energy of formation of thiophene as a function of temperature calculated by use of these results.

Combustion Calorimetry.—Part of the same highly purified sample of thiophene used in the earlier study[2] was also used for the study reported here. The apparatus and method have been described elsewhere.[4] A summary of the calorimetric results is given in Table I. The last column of the table gives the experimentally determined values of $\Delta U_c^\circ/M$, the change in internal energy at 25° per gram mass of thiophene, for the idealized combustion reaction (eq. 1)

$$C_4H_4S(l) + 13/2O_2(g) + 49H_2O(l) \longrightarrow 4CO_2(g) + H_2SO_4{\cdot}50H_2O(l) \quad (1)$$

in which each reactant and product is in its appropriate standard state.[5]

The combustions were carried out in the platinum-lined bomb, Pt-4.[4] The samples were contained in Pyrex ampoules. Ten grams of water was initially added to the bomb. The air originally present in the bomb was not removed when the bomb was charged with oxygen. Each combustion was initiated at 23.00°, and the quantities of thiophene and auxiliary oil (Sample USBM-P3$_a$) were chosen to produce a 2° temperature rise in the calorimeter. When 60% of the expected rise in temperature had been reached, rotation of the bomb was started. The bomb was rotated for 90 seconds.

The energy equivalent of the calorimetric system, $\mathcal{C}_{\text{eff.}}$ (calor.), was determined by six combustions of benzoic acid (National Bureau of Standards Sample 39g). The precision of the energy equivalent determinations was unusually good—standard deviation of the mean, 0.002%.

In addition to the experiments shown in the table, three others were carried out. After the first experiment, a significant amount of carbon was found occluded in the partially fused remnant of the stem of the Pyrex ampoule. After the fourth experiment, SO_2 was found in the discharge gases of the bomb. It is probable that in charging the bomb for this experiment some of the air (necessary for complete oxidation of the sulfur to its +6 valence state) was inadvertently removed. After the fifth experiment, the presence of shattered glass and a large amount of carbon in the bomb indicated a violent rupture of the ampoule when the charge in the bomb was fired, accompanied probably by loss of sample from the crucible.

Table II gives the values for (a) the change in internal energy, ΔU_c°, of the idealized combustion reaction (eq. 1); (b) the enthalpy change, ΔH_c°, of the same reaction; (c) the standard heat of vaporization, $\Delta H_{\text{vap.}}^\circ$ (data of ref. 2 extrapolated to 25° and corrected for gas imperfection); and (d) the standard heat of formation, ΔH_f°, of thiophene in both the liquid and ideal gas states (eq. 2).

$$4C(c, \text{graphite}) + 2H_2(g) + S(c, \text{rhombic}) \longrightarrow C_4H_4S(l, \text{ or } g) \quad (2)$$

The table also includes values of ΔH_f° of the liquid obtained by Sunner and Lundin,[6] Moore, Renquist and Parks[7] and Franklin and Lumpkin,[8] and the value obtained previously in this Laboratory.[2] The

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(1) This investigation was part of American Petroleum Institute Research Project 48A on "The Production, Isolation and Purification of Sulfur Compounds and Measurement of their Properties," which the Bureau of Mines conducts at Bartlesville, Okla., and Laramie, Wyo.

(2) G. Waddington, J. W. Knowlton, D. W. Scott, G. D. Oliver, S. S. Todd, W. N. Hubbard, J. C. Smith and H. M. Huffman, This Journal, **71**, 797 (1949).

(3) H. M. Huffman and E. L. Ellis, *ibid.*, **57**, 41 (1935).

(4) W. N. Hubbard, C. Katz and G. Waddington, *J. Phys. Chem.*, **58**, 142 (1954).

(5) W. N. Hubbard, D. W. Scott and G. Waddington, *ibid.*, **58**, 152 (1954).

(6) S. Sunner and B. Lundin, University of Lund, Lund Sweden, unpublished measurement.

(7) G. E. Moore, M. L. Renquist and G. S. Parks, This Journal, **62**, 1505 (1940).

(8) J. L. Franklin and H. E. Lumpkin, *ibid.*, **74**, 1023 (1952).