falls from 1.054 at 25° to 1.014 at 323°.[6] At 600° it would probably be even smaller. Perhaps an isotopic exchange takes place at lower temperatures before the carbon dioxide and steam are separated, but if such an exchange takes place, it would have to be catalyzed by products formed in the combustion since a simple mixing of carbon dioxide and steam for a short period of time produces no isotopic exchange.[1] The magnitude of the effect, about 4 p. p. m. in terms of water density, is small enough to be accounted for by such an exchange and it is in the direction expected.

Acknowledgments.—We are greatly indebted to Dr. D. L. Tabern of the Abbott Laboratories for supplying the halibut liver oil residues, to Mr. Stanley Cristol for carrying out the combustion of the oil, to Mr. J. L. Gabbard for the loan of the electrolysis cells, and to Mr. B. Z. Wiener for carrying out the second electrolysis mentioned in Table II.

Summary

Cholesterol has been examined for its deuterium content, but after all the necessary corrections have been applied to the data it appears that the deuterium content of cholesterol is normal. The measurements indicate a slight deficiency of heavy hydrogen, but the magnitude of the deficiency is hardly greater than the experimental error. Halibut liver oil residues have also been analyzed isotopically, but again the hydrogen appears to be normal in its deuterium content.

We have found, however, that there is a marked fractionation of the oxygen isotopes on combustion of the cholesterol.

EVANSTON, ILL. RECEIVED SEPTEMBER 21, 1936

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[6] H. C. Urey and Lotti J. Greiff, THIS JOURNAL, 57, 321 (1935).

[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICAL CHEMISTRY, THE UNIVERSITY OF LIVERPOOL]

The Reactivity of Hydrogen Peroxide in Bromine–Bromide Solutions

BY ROBERT OWEN GRIFFITH AND ANDREW MCKEOWN

A recent paper by Livingston and Schoeld[1] on the photochemical behavior of H_2O_2–HBr–Br_2 mixtures in aqueous solution prompts us to communicate briefly the results of some experiments which we carried out in 1933–34 on this same system, especially as (a) our conclusions regarding the photochemical reaction are diametrically opposed to those of Livingston and Schoeld, and (b) our observations on the thermal reaction differ in some respects from those of Bray and Livingston.[2]

Dealing first with the thermal reaction, we find that H_2O_2–HBr–Br_2 systems at constant temperature and in the dark never attain "steady state" conditions as defined by Bray and Livingston, that is, the concentration of bromine $[\Sigma Br_2]$, and correspondingly that of hydrobromic acid, never reach stationary values so long as any hydrogen peroxide remains undecomposed. According to our measurements, if no bromine is originally present in the system, $[\Sigma Br_2]$ at first rapidly increases toward a pseudo-stationary value, but instead of remaining at this value it then slowly but progressively increases with diminishing concentration of hydrogen peroxide. If excess of bromine is originally present, $[\Sigma Br_2]$ at first rapidly falls to a pseudo-stationary value, passes through a minimum, and then as before slowly increases. In either case, provided the sum $[HBr] + {}^1/_2[\Sigma Br_2]$ has the same value and provided enough hydrogen peroxide be present initially, the concentration of bromine becomes after a sufficient lapse of time the same function of the hydrogen peroxide concentration, independent of the previous history of the system.

For our experiments we have employed, with identical results, hydrogen peroxide from the following sources: (1) Merck 30% Perhydrol free from preservatives, (2) a preparation from sodium peroxide following the method of Rice, Rieff and Kirkpatrick,[3] and (3) a sample obtained from an A. R. hydrogen peroxide by distillation under reduced pressure. Our measurements of bromine concentration were carried out (α) analytically by the method described by Bray and Livingston,[2] and (β) spectrophotometrically.

Table I gives the results of four typical experiments. It will be noted that, after the attainment of pseudo-stationary conditions, the con-

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[1] Livingston and Schoeld, THIS JOURNAL, 58, 1244 (1936).

[2] Bray and Livingston, *ibid.*, 45, 1264 (1923).

[3] Rice, Rieff and Kirkpatrick, *ibid.*, 48, 3019 (1926).

TABLE I

Temp. = 20°; $[HBr]_{init.}$ = 0.202 *M*; $[\Sigma Br_2]_{init.}$ = 0.004 *M*

Merck's $[H_2O_2]_{init.}$ = 0.40 *M*

$[H_2O_2]$	$[\Sigma Br_2]_{anal.}$	$[\Sigma Br_2]_{phot.}$	$k_{uni.} \times 10^6$
0.337	0.00332	0.00323	695
.147	.00361	.00369	678
.054	.00406	.00416	663
.021	.00436	.00446	641
.008	.00446	.00456	

Synthetic $[H_2O_2]_{init.}$ = 0.54 *M*

$[H_2O_2]$	$[\Sigma Br_2]_{anal.}$	$[\Sigma Br_2]_{phot.}$	$k_{uni.} \times 10^6$
0.239	0.00344	0.00341	682
.089	.00383	.00387	668
.033	.00420	.00432	660
.013	.00448	.00449	...
.002	.00465	.00472	

Temp. = 20°; $[HBr]_{init.}$ = 0.1616 *M*; $[\Sigma Br_2]_{init.}$ = 0.0011 *M*

Synthetic $[H_2O_2]_{init.}$ = 0.38 *M*

$[H_2O_2]$	$[\Sigma Br_2]_{phot.}$	$k_{uni.} \times 10^6$
0.335	0.00091	456
.189	.00102	447
.092	.00119	442
.052	.00131	436
.026	.00145	...
.002	.00168	

Distilled $[H_2O_2]_{init.}$ = 0.4 *M*

$[H_2O_2]$	$[\Sigma Br_2]_{phot.}$	$k_{uni.} \times 10^6$
0.360	0.00095	458
.213	.00103	449
.114	.00117	442
.028	.00144	431
.017	.00153	

centration of bromine steadily increases in every case; in some of our experiments the increase in $[\Sigma Br_2]$ amounts to more than 100%. The rate of increase of $[\Sigma Br_2]$ with time (beyond the pseudo-stationary state) is practically a constant in each experiment while the hydrogen peroxide concentration changes over the range 0.3 ⟶ 0.03 *M*. When the hydrogen peroxide becomes very weak, however, $d[\Sigma Br_2]/dt$ falls off in each case. For the two concentrations of hydrobromic acid in Table I the constant rate $d[\Sigma Br_2]/dt$ equals 31 and 9.3 $\times 10^{-8}$ moles per minute, respectively, and from other experiments not listed this rate appears to be roughly proportional to the fifth power of [HBr].

Attention may also be directed to a further point. The last column for each experiment gives values of $k_{uni.}$ (natural logs; time in minutes) for the rate of disappearance of hydrogen peroxide, *viz.*, $-d[H_2O_2]/dt = k_{uni.}[H_2O_2]$. It will be seen that $k_{uni.}$ falls with time, that is, with diminishing $[H_2O_2]$. The fall is considerably greater than that which might be due to the slight decrease in the concentration of hydrobromic acid resulting from the increasing concentration of bromine. Thus in the first experiment [HBr] decreases about 1%, but $k_{uni.}$ falls by 8%. We have observed this fall in $k_{uni.}$ in all our experiments and we believe it to be real and of significance for the mechanism of the reaction.

We have also studied the photochemical behavior of H_2O_2–HBr–Br_2 systems from various aspects. One of the methods employed was to allow a H_2O_2–HBr–Br_2 mixture to attain, at constant temperature and in the dark, a pseudo-stationary state in which under our experimental conditions $[\Sigma Br_2]_d$ is changing but slowly, then illuminate with monochromatic light and measure by photometric means (thermopile–galvanometer) the *initial* rate of disappearance of bromine. The apparatus used was similar to that of Griffith, McKeown and Winn[4] the main difference being that e. m. fs. generated in the thermopile were balanced by a compensator, similar to that described by Goodeve and Nagai,[5] and recorded on a Weston precision millivoltmeter used in conjunction with a Zernicke *Zc* galvanometer. The thermopile was standardized by means of the uranyl oxalate reaction and checked with a carbon filament lamp standardized by the N. P. L. Table II gives the results (γ = quantum yield, molecules of bromine disappearing per quantum absorbed) of six experiments using blue light (λ = 436 mμ).

TABLE II

$[H_2O_2]$	$[\Sigma Br_2]_d$	Quanta absorbed per minute	Molecules of Br_2 disappearing per minute *initially*	γ
Temp. = 20°; $[HBr]_{init.}$ = 0.1437; $[\Sigma Br_2]_{init.}$ = 0; 2-cm. cell				
0.15	0.000523	2.04×10^{16}	1.61×10^{17}	7.9
.15	.000523	4.14×10^{15}	4.74×10^{16}	11.5
.042	.000714	2.17×10^{16}	4.42×10^{16}	2.0
.042	.000714	4.67×10^{15}	1.53×10^{16}	3.3
Temp. = 17°; $[HBr]_{init.}$ = 0.1071; $[\Sigma Br]_{init.}$ = 2×10^{-4}; 10-cm. cell				
0.19	0.0001194	2.57×10^{16}	4.4×10^{17}	17
.19	.0001194	5.66×10^{15}	1.9×10^{17}	34

The data show that quantum yields considerably in excess of unity are obtained, and that γ is roughly proportional to $[H_2O_2]$ and increases with decreasing light intensity. On these grounds there appears therefore to be no doubt that the photochemical action between hydrogen peroxide and bromine is a chain reaction.

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(4) Griffith, McKeown and Winn, *Trans. Faraday Soc.*, **29**, 369 (1933).

(5) Goodeve and Nagai, *ibid.*, **27**, 508 (1931).

Results analogous to the above were also obtained by a method similar to that used by Livingston and Schoeld. A photostationary state (denoted by suffix *l*) was attained from a given pseudo-stationary state in the dark (suffix *d*) by illumination with monochromatic light of constant intensity. Both $[\Sigma Br_2]_d$ and $[\Sigma Br]_l$ were measured photometrically. On the basis of the Bray–Livingston mechanism for the thermal reaction, it can easily be shown, from the condition that the rate of formation of bromine equals its rate of disappearance both for the thermal and for the photostationary state, that the purely photochemical reaction of hydrogen peroxide and bromine is given by

$$\left\{-\frac{d[\Sigma Br_2]}{dt}\right\}_{\text{phot.}} = \frac{1}{2}\,k_{\text{uni.}}\,[H_2O_2]\left\{\frac{[H^+]_l[Br^-]_l}{[H^+]_d[Br^-]_d} - \frac{[H^+]_d[Br^-]_d[\Sigma Br_2]_l\{K_3 + [Br^-]_d\}}{[H^+]_l[Br^-]_l[\Sigma Br_2]_d\{K_3 + [Br^-]_l\}}\right\} \qquad (1)$$

where K_3 is the equilibrium constant of tribromide formation. From a knowledge of the energy absorbed in the photo-stationary state the quantum yield can therefore be calculated. Table III gives the results of a few experiments of this type.

TABLE III

Temp. = 17°; λ = 436 mμ

$[\Sigma Br_2]_d$	$[\Sigma Br_2]_l$	Quanta absorbed per minute	Molecules of Br_2 disappearing per minute	γ
$[H_2O_2] = 0.167$; $[HBr]_{\text{init.}} = 0.149$; $k_{\text{uni.}} = 2.9 \times 10^{-4}$; 2-cm. cell				
0.000715	0.000088	5.41×10^{15}	4.33×10^{16}	8
.000715	.000231	2.81×10^{15}	3.36×10^{16}	12
$[H_2O_2] = 0.19$; $[HBr]_{\text{init.}} = 0.1071$; $[\Sigma Br_2]_{\text{init.}} = 2 \times 10^{-4}$; $k_{\text{uni.}} = 1.53 \times 10^{-4}$; 10 cm. cell				
0.0001194	0.0000179	4.59×10^{15}	1.18×10^{17}	26
.0001194	.0000414	2.25×10^{15}	0.91×10^{17}	40

It will be remarked that at the bromine concentrations and light intensities employed, the photostationary concentration of bromine has been reduced as much as eight-fold below the thermal value. This is in marked contrast with the much smaller relative changes in bromine concentration effected by Livingston and Schoeld, these authors using higher concentrations of bromine and green light which is less strongly absorbed than blue. However, the much smaller quantum yields recorded by them are not wholly to be ascribed to these differences. Our method of calculating the photochemical action at the photostationary state is quite different from that used by Livingston and Schoeld, who write

$$\{-d[\Sigma Br_2]/dt\}_{\text{phot.}} = (k_l - k_d)[H_2O_2] \qquad (2)$$

where k_l and k_d are the (measured) unimolecular constants of decomposition of hydrogen peroxide in the light and dark, respectively. There appears, however, to be no theoretical justification for this relation even as an approximation, and indeed a closer scrutiny of their data shows that equation (2) must give far too low an estimate of the photochemical action. Thus, in their experiment 2 where $[\Sigma Br_2]$ has been reduced by the light from 0.0008 to 0.0005, that is, by 38%, it is obvious that approximately this same fraction of that reaction which uses up bromine in the thermal stationary state must now in the light be replaced by photochemical action. The reaction forming bromine in the dark is given by $^1/_2k_d[H_2O_2]$, hence the photochemical action is, at least as regards order of magnitude, about 19% of $k_d.[H_2O_2]$ and not 2% as taken by Livingston and Schoeld. Recalculation of their data for experiments 2, 4, 7, 10, 13 and 16 on the basis of equation (1) leads to $\gamma = 5.1$, 1.9, 1.8, 1.8, 2.4 and 0.46, respectively, in place of the recorded values 0.68, 0.34, 0.48, 0.26, 0.70 and 0.34. There seems little doubt therefore that, even with green light as used by Livingston and Schoeld, quantum yields greater than unity can be obtained, especially for low values of the energy absorbed.

The evidence presented above shows that under both thermal and photochemical conditions the kinetics of H_2O_2–HBr–Br_2 mixtures are likely to be of complex character. Photochemically, chain reactions must occur involving Br atoms and probably radicals such as HO_2 and OH. Under thermal conditions, while doubtless the excellent work of Bray and his co-workers has elucidated the main outlines of the kinetics, additional processes must be assumed to occur in order to explain the absence of a true stationary state. It seems likely that it is the reaction between hydrogen peroxide and bromine which—thermally as well as photochemically—is of complex nature. We do not wish, however, to discuss the mechanism further at present, as we are continuing our study of these reactions and hope to be able to publish a more detailed report in the near future.

Summary

1. Data are presented to show that for H_2O_2–HBr–Br_2 mixtures in aqueous solution, the "stationary state" characteristic of the Bray–Livingston mechanism for the thermal reaction does not in fact occur.

2. The photochemical reaction of hydrogen

peroxide and bromine under the influence of blue light gives quantum yields considerably in excess of unity. A recalculation of Livingston and Schoeld's data gives quantum yields greater than unity for green light also. A chain mechanism is indicated, contrary to the conclusion of Livingston and Schoeld.

LIVERPOOL, ENGLAND RECEIVED AUGUST 29, 1936

[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Viscosity of Aqueous Solutions of Electrolytes as a Function of the Concentration. IV. Potassium Ferrocyanide

BY GRINNELL JONES AND ROBERT ELIOT STAUFFER

Introduction

This paper describes a continuation of the earlier researches[1] carried out in this Laboratory on the viscosity of solutions of electrolytes. An historical introduction and a discussion of the general objects of the investigation and the progress already made will be found in the earlier papers of this series and is therefore omitted here. In this paper the investigation is extended to a salt of a higher valence type and measurements are made at both 25 and 0° on the same solution in order to permit the study of the influence of temperature on the phenomena. Potassium ferrocyanide was selected as the most suitable unitetravalent salt since it is sufficiently soluble and stable and is only slightly hydrolyzed. Moreover, measurements on viscosity were needed for use in the interpretation of data on the conductance of this salt which were being obtained in this Laboratory (see the following paper).

Experimental

The apparatus and experimental procedure was the same as that described in the earlier papers with some modifications and improvements in detail. The most important innovation was the construction of an ice thermostat permitting the viscometer to be placed in succession in the 25 and 0° thermostats so that measurements could be made in succession on the same solution.

The ice thermostat consisted of a tank of about 180-liter capacity firmly supported on a three-point support of Monel metal and surrounded on all sides except the top with diatomaceous earth at least 8 cm. thick. The top had insulating covers built in sections permitting temporary removal in parts when necessary to insert the viscometers or to add fresh ice. The tank had small double windows of plate glass in front and rear to permit observation and operation of the optical system necessary for the automatic timing described in the earlier papers. The thermostat when in use was filled with a well-stirred mixture of ice and water. Wire screens of 14-mesh were arranged as near to the viscometer as possible to protect the fragile instrument from fracture by the moving ice and also to keep open narrow paths for the beam of light needed for operation of the automatic timing system and for inspection of the upper bulb of the viscometer. Water was kept circulating vigorously through the ice and around the viscometer by three motor-driven stirrers. A very good thermometer having an open scale 6 cm. long per degree was mounted totally immersed near the viscometer and read through the window to thousandths of a degree by a telescope. The readings of the thermometer and the consistency of the viscometric data prove that our thermostat can maintain a temperature safely within 0.003 of 0°. It requires about 50 pounds (25 kg.) of ice per day in hot summer weather.

Our old instrument has an inconveniently long period at 0° and therefore a new viscometer of vitreous silica was constructed with a slightly wider capillary (0.052 cm. diameter and 17.9 cm. long) and therefore a shorter period (428.7 sec. for water at 25° and 862.9 sec. for water at 0°). The ice thermostat had its own optical system, photoelectric cell and amplifiers but the same chronograph and clocks served both thermostats. Three different viscometers could be used interchangeably in either thermostat and measurements with different instruments could be going on simultaneously in both thermostats if desired.

The best potassium ferrocyanide available by purchase was twice recrystallized by dissolving in water at 60°, cooling and adding ethyl alcohol, followed by centrifugal drainage. It was dried by heating to 90° in nitrogen at low pressure for several hours. The solutions were made up by weight.

The experimental data at 25 and at 0° are recorded in Tables I and II, respectively. The values for the density given in parentheses were not actually measured but were computed by the formula given below. The third column gives the relative viscosity before applying the kinetic energy correction, which is shown in column 4. The relative viscosity after applying the kinetic energy correction is given in column 5. In some cases a small correction was necessary to bring the data to a round concentration. The results after applying this correction are shown in the last column.

Interpretation of the Data.—The experimental data given below on the density of potassium

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[1] Grinnell Jones and M. Dole, THIS JOURNAL, 51, 2950 (1929); Grinnell Jones and S. K. Talley, *ibid.*, 55, 624, 4124 (1933); *Physics*, 4, 215 (1933); Grinnell Jones and H. J. Fornwalt, THIS JOURNAL, 57, 2041 (1935); 58, 619 (1936).