The *p*-bromophenacyl tetraester melted at 170–171°.

Anal. Calcd. for $C_{40}H_{30}O_{12}SBr_4$: C, 45.5; H, 2.85; S, 3.04; Br, 30.4. Found: C, 45.6; H, 2.92; S, 3.24; Br, 30.6.

NORTHERN REGIONAL RESEARCH LABORATORY
PEORIA, ILLINOIS

Function of Organic Material in the Photochemical Formation of Hydrogen Peroxide at Zinc Oxide Surfaces[1]

BY CHARLES B. VAIL, JAMES P. HOLMQUIST AND LOCKE WHITE, JR.

RECEIVED AUGUST 28, 1953

The photochemical formation of hydrogen peroxide in aqueous zinc oxide suspensions has been the subject of several investigations,[2–6] including the recent works of Markham and Laidler[7] and Rubin, Calvert, Rankin and MacNevin.[8] In each of these cases the effectiveness of certain organic materials to increase the yield of peroxide was noted and some efforts were made to determine the function of those materials. Most authors have considered the additives as reactants, rather than peroxide stabilizers, and have supported that contention with experimental evidence of oxidation of the additive. Markham and Laidler, for example, reported the formation of catechol in suspensions containing phenol, and Rubin, *et al.*, recovered carbon dioxide from potassium oxalate suspensions. In no case, however, has there been a quantitative proof that the additive participates directly in the peroxide reaction. The objective of this research was to establish the fate of the additive and the stoichiometry of the reactions involved.

Previous investigations have used, for the most part, relatively complex molecules such as phenols, acetanilide, etc. The effectiveness of these materials is satisfactory, but so many oxidation products can be derived from any one that an analysis of the irradiated suspension is difficult at best. A more desirable additive would be a compound such as an oxalate or formate which has only one normal oxidation product. Fortunately, such compounds are effective[8] and actually produce greater yields than most others. Furthermore, they were both readily available with carbon-14 labeling which greatly facilitated the tracing of their fate.

Experimental Procedure

The chemicals used were reagent grade; the zinc oxide was J. T. Baker Analyzed. In all experiments redistilled water, freed of carbon dioxide, was employed. Commercial cylinder oxygen and water-pumped nitrogen were used with no further purification.

The light source was a General Electric A-H6 lamp operated from a d.c. power supply. A fairly narrow band of light was isolated around 366 mμ by means of Corning glass filters No. 7380 and 5860.

Reactions were carried out in a Pyrex cell which rather resembled a gas washing bottle. The lower half, however, was made from a large test-tube provided with a flat window near the bottom. The reaction mixture, 0.5 g. of ZnO in 85 ml. of solution, was placed in the cell along with a magnetic stirrer bar, and the assembled vessel was fastened together securely.

The irradiation period was preceded by five minutes of equilibration during which oxygen was bubbled into the stirred suspension at about 100 ml./min. After equilibration the exit tube atop the reaction cell was connected by rubber tubing to a filter stick immersed in dilute sodium hydroxide, and irradiation was commenced. Upon completion of the irradiation period, which ranged from one to three hours, 35 ml. of dilute HCl was introduced from a vessel inserted in the inlet line to the cell. The resulting acid solution was warmed and swept with nitrogen for 30 minutes. Inactive Na_2CO_3 was then added as carrier to the $C^{14}O_2$ absorbed in the alkali, and the combined carbonates were precipitated as $BaCO_3$. The dried $BaCO_3$ was used for radioactivity measurements.

Determinations of the radioactivity were made in accordance with the gas-phase procedure of Skipper, Bryan, White and Hutchison.[9] A few of the "high" activity samples from oxalate runs were measured on planchets with a Nuclear Measurements Corporation proportional counter. In both instances the total count, not the specific activity, was sought. Blank runs were made by the same procedure without irradiation, and the activities of the irradiated runs were corrected accordingly. The activities of the blanks never exceeded 5% of those for the runs. The yield of CO_2 was calculated from the net total count and the specific activity of the initial additive solution. To determine the latter value an aliquot of the solution was oxidized to CO_2 by a wet oxidation procedure[10] and then assayed by the method described above.

The analysis for hydrogen peroxide was made with a portion of the residual acid solution according to the colorimetric (titanium sulfate) procedure of Eisenberg.[11] The oxalate ion, however, was found to intensify the color of the titanium complex in rough proportion to the oxalate concentration. Standardization curves, therefore, were prepared for each concentration.

Isotopic Exchange.—In the initial planning of this work, consideration was given to a possible isotopic exchange of carbon atoms between the labeled additive and inactive CO_2 accidentally incorporated in the system. The low activity of the blanks, however, showed that if exchange did occur, there was very little CO_2 present to participate. Nevertheless, the possibility existed that larger and variable amounts of inactive CO_2 might accidentally contaminate other samples. Therefore, the exchange was investigated.

Solutions of 0.01 *M* NaO_2CH and 0.01 *M* C-14 enriched Na_2CO_3 were mixed and agitated vigorously. Aliquots were withdrawn periodically and precipitated as $BaCO_3$. The $BaCO_3$ was assayed for radioactivity by the procedures described above. The results, shown in Table I, indicate that no significant exchange occurred even in 72 hours.

TABLE I

Time, hr.	Specific activity of Na_2CO_3, μc./mole	Time, hr.	Specific activity of Na_2CO_3, μc./mole
0	1.00	3	1.00
5 (min.)	0.95	5	0.98
0.5	.92	7	.98
1	.98	24	.97
2	.98	72	.96

There is some deviation from the initial activity, yet there is no clearly defined trend. The deviations may have been

---

[1] This work was supported by the Charles F. Kettering Foundation.

[2] C. Winther, *Z. Wiss. Phot.*, **21**, 141, 168, 175 (1921).

[3] E. Baur and G. Neuweiler, *Helv. Chim. Acta*, **10**, 901 (1927).

[4] G. Goodeve, *Trans Faraday Soc.*, **33**, 340 (1937).

[5] K. Yamahuzi, M. Nisioeda and H. Imagawa, *Biochem. Z.*, **301**, 404 (1939).

[6] C. N. Chari and M. Qureshi, *J. Indian Chem. Soc.*, **21**, 97, 297 (1944).

[7] M. C. Markham and K. J. Laidler, *J. Phys. Chem.*, **57**, 363 (1953).

[8] T. Rubin, J. G. Calvert, G. T. Rankin and W. MacNevin, THIS JOURNAL, **75**, 2850 (1953).

[9] H. E. Skipper, C. E. Bryan, L. White, Jr., and O. S. Hutchison, *J. Biol. Chem.*, **173**, 371 (1948).

[10] A. Lindenbaum, J. Schubert and W. D. Armstrong, *Anal. Chem.*, **20**, 1120 (1948).

[11] G. M. Eisenberg, *Ind. Eng. Chem., Anal. Ed.*, **15**, 327 (1943).

incurred by accidental exposure of the samples to air during the processing, for a $CO_3^{=}$–CO_2 exchange does occur on moist carbonate. It is significant, furthermore, that the sodium formate exhibited no activity. The experiment was repeated using labeled formate and inactive carbonate, and in this series no activity was transferred to the carbonate.

Results and Discussion

The yield of peroxide varies considerably with the additive concentration and it seemed appropriate to investigate the reaction over a wide range of concentrations. The results are shown in Tables II and III.

TABLE II

PHOTOLYSIS PRODUCTS IN THE SODIUM FORMATE SUSPENSION

NaO_2CH, moles/l.	Yield of peroxide, moles × 10^5	Yield of CO_2,[a] moles × 10^5	Formate oxidized/ peroxide formed
6.0×10^{-1}	7.1	7.2	1.0
	6.5	7.0	1.1
1.5×10^{-1}	10.1	10.2	1.0
	6.6	6.1	0.9
1.23×10^{-2}	5.7	6.0	1.1
	5.9	6.0	1.0
1.23×10^{-3}	3.8	4.0	1.1
	3.8	4.1	1.1
	3.8	4.2	1.1
1.23×10^{-4}	1.1	0.9	0.8
	1.1	1.0	0.9
	1.0	1.0	1.0
1.23×10^{-5}	0.8	0.3	0.4
	0.8	0.1	0.1
	0.8	0.1	0.1

[a] Based on the specific activity of sodium formate = 43.8 μc./mole.

TABLE III

PHOTOLYSIS PRODUCTS IN THE POTASSIUM OXALATE SUSPENSION

$K_2C_2O_4$, moles/l.	Yield of peroxide, moles × 10^5	Yield of CO_2,[a] moles × 10^5	Oxalate oxidized[b]/ peroxide formed
1.02×10^{-1}	6.2	20.0	1.6
	5.8	20.0	1.7
1.02×10^{-2}	3.2	13.0	2.0
	4.0	12.4	1.5
	4.5	10.2	1.2
1.02×10^{-3}	2.3	5.2	1.1
	2.3	5.8	1.3
	2.4	5.4	1.1
1.02×10^{-4}	0.75	1.4	0.9
	1.0	1.8	0.9
	0.8	1.6	1.0
1.02×10^{-5}	0.5	0.2	0.2
	0.6	0.2	0.2

[a] Based on specific activity of potassium oxalate = 789 μc./mole. [b] Each mole of oxalate yields two moles of CO_2.

The production of $C^{14}O_2$ confirmed the oxidation of the formate and oxalate during the synthesis of hydrogen peroxide. The mole-for-mole oxidation (column 4), furthermore, proves clearly that the yield of peroxide is dependent on the reductive properties of these compounds. The possibility that the additive may be oxidized only in a subsequent reaction with the peroxide seems very remote in view of the exact stoichiometric relationship at various yields of peroxide, particularly in the formate case. The mole ratio of one with formate persists, furthermore, from 0 to 30°, a condition very unlikely to exist if independent thermal (oxidation) and photochemical (formation) reactions were involved.

The stoichiometric relationship with both additives falls considerably below unity at the lowest concentration (10^{-5} *M*) which might indicate a limited yield of H_2O_2 without additive participation. Indeed, approximately the same peroxide yield is obtained in "additive-free" suspensions. It seems more probable, however, that oxidizable impurities account for the small non-additive yields and for the excess in the dilute additive solutions. The presence of impurity is indicated by the observation that this zinc oxide darkens if heated *in vacuo*, but not if preheated in an oxygen atmosphere. Also, commercial oxygen supplies are known to contain some hydrocarbon impurities.[12] The reaction has not been studied under conditions which meticulously avoid contamination from sources such as the foregoing. Accordingly, no definite conclusion can be reached concerning the dilute and the non-additive systems, and no previous observation can be regarded as reliable proof that peroxide can be produced in the absence of oxidizable matter.

At the higher concentrations of oxalate the mole ratios indicate excessive oxidation of the oxalate, but this is not unexpected in view of the photosensitive properties of oxalates. It was found, furthermore, that the light can induce a reaction between the peroxide and additive resulting in the increased mole ratio.

A third organic additive, ethanol, was studied as a sort of prototype of the compounds with several oxidation products. The tracer technique, however, did not prove very useful in this case. Ethanol is apparently not oxidized to CO_2; indeed, no oxidation product was definitely established by radioactivity techniques. In separate procedures the attempted recovery of (a) acetaldehyde by precipitation with 2,4-dinitrophenylhydrazine, and (b) acetic acid by evaporation of the filtered reaction mixture (rendered alkaline) resulted in samples with negligible or unreproducible activities. It is not legitimate, therefore, to state categorically that all additives participate as do the oxalate and formate, even though all other indications[7,8] including the foregoing studies suggest that they do.

Acknowledgment.—The authors wish to thank Miss Linda Simpson for making the radioactivity measurements reported in this paper.

[12] L. A. Wooten and W. A. Guldner, *Anal. Chem.*, **14**, 835 (1942).

SOUTHERN RESEARCH INSTITUTE
BIRMINGHAM 5, ALABAMA

2-Pyrones. VII. 2-Pyridones from 2-Pyrones

BY RICHARD H. WILEY, L. H. KNABESCHUH, A. L. DUCKWALL AND N. R. SMITH

RECEIVED JULY 27, 1953

In a previous paper[1] we presented data on the preparation and properties of some 5-carboxy-2-

[1] R. H. Wiley, N. R. Smith and L. H. Knabeschuh, THIS JOURNAL, **75**, 4482 (1953).