Photoinduced Oxidation of Benzoic Acid with Aqueous Hydrogen Peroxide

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The photodecomposition of benzoic acid in aqueous hydrogen peroxide has been studied. When the ratio $[H_2O_2]_0/[PhCO_2H]_0$ is low, the decomposition of benzoic acid and hydrogen peroxide stops during irradiation, while at a high $[H_2O_2]_0/[PhCO_2H]_0$ ratio, benzoic acid is completely decomposed with cleavage of the aromatic ring. Hydroxybenzoic acid is a major product, and benzene and phenol are minor products during the initial stages of oxidation. Later lower aliphatic acids such as malonic acid appear. The probable mechanism for decomposition is discussed on the basis of product yields.

PHOTO-OXIDATION of benzene in aqueous solution proceeds *via* benzvalene to give cyclopenta-1,3-dienecarbaldehyde, which has no aromatic ring.[1,2] On the other hand, in the presence of H_2O_2, HO• radical formed by the decomposition of H_2O_2 reacts with benzenes to form phenols and biphenyls, where the product distribution depends on the acidity of the solution.[3,4]

Carboxylic acids decompose with evolution of CO or CO_2 in direct photolysis,[5] *e.g.* the vapour phase photolysis of benzoic acid gives CO_2 and benzene as main products and CO as a minor product.[6] In the presence of H_2O_2, it is expected that hydroxylation of the aromatic ring by HO• radicals would compete with decarbonylation or decarboxylation of benzoic acid. Hydroxylation products should be more reactive than benzoic acid itself towards the HO• radical.[7] Therefore, at a high concentration of H_2O_2, cleavage of the aromatic ring may occur as well as the oxidation of phenols or catechols by peracetic acid.[8-10]

The present study reports the complete H_2O_2 oxidation of benzoic acid in connection with the removal of pollutants in waste water by photo-oxidation with H_2O_2. The mechanism of cleavage of the aromatic ring will be discussed by studying the oxidation and cleavage products.

RESULTS AND DISCUSSION

In order to find optimum conditions for the complete oxidation of benzoic acid, the effects of the initial molar concentration ratio, $[H_2O_2]_0/[PhCO_2H]_0$, and light wavelength (a quartz vessel, runs 1, 2a, 3, 4, 5a, and 6, or Pyrex vessel, runs 2b and 5b) on the decomposition of benzoic acid were examined preliminarily. The initial concentration of benzoic acid was 1.5—2.5 × 10^{-2}M and a Halos 300 W high-pressure mercury lamp was used as a light source. The estimation of H_2O_2 concentration was done iodometrically and that of benzoic acid was performed with g.l.c.

In the absence of H_2O_2 (run 1), decomposition of benzoic acid in aqueous solution did not occur after irradiation for 20 h. Therefore, H_2O_2 was necessary for the decomposition of benzoic acid in aqueous solution. Furthermore, perbenzoic acid which is expected from the acid-catalysed reaction of benzoic acid with H_2O_2 was not detected iodometrically[11] after 20 h (run 5c, $[H_2O_2]_0/[PhCO_2H]_0$ 24.5). This fact suggests that $PhCO_3H$ does not participate in this photolysis.

Light of < 290 nm is absorbed by our Pyrex vessel but not by a quartz vessel. In addition, the extinction coefficient of H_2O_2 is 23 at 250 nm, 0.94 at 300 nm, and 0.36 at 315 nm, and that of $PhCO_2H$ is 630 at 250 nm, 0.33 at 300 nm, and nearly zero at 315 nm. Therefore, only H_2O_2 should decompose in a Pyrex vessel, while both H_2O_2 and $PhCO_2H$ should be excited in quartz [equations (1) and (2)]. Excited $PhCO_2H$, $[PhCO_2H]^*$, may then transfer energy to H_2O_2 [equations (3) and (4)]. The rates of decomposition of both $PhCO_2H$ and H_2O_2 in quartz were about twice that in Pyrex, but product yields were not affected by the nature of the vessel except for the yield of PhOH (see below). Therefore, a quartz vessel was used.

$$H_2O_2 \xrightarrow{h\nu\text{(Pyrex or quartz)}} [H_2O_2]^* \longrightarrow 2HO\cdot \qquad (1)$$

$$PhCO_2H \xrightarrow{h\nu\text{(quartz)}} [PhCO_2H]^* \qquad (2)$$

$$[PhCO_2H]^* + H_2O_2 \longrightarrow PhCO_2H + [H_2O_2]^* \qquad (3)$$

$$[H_2O_2]^* \longrightarrow 2HO\cdot \qquad (4)$$

Figure 1 shows the decomposition of H_2O_2 and $PhCO_2H$ in runs 2a, 4, and 5a, where run 3 ($[H_2O_2]_0/[PhCO_2H]_0$ 4.5) was eliminated in view of the observation of the same tendency as runs 2a and 4. In run 2a ($[H_2O_2]_0/[PhCO_2H]_0$ 1.3), as the decomposition of H_2O_2 proceeded, the colour of the solution turned yellow and then dark brown; thereafter no further decomposition of H_2O_2 or $PhCO_2H$ occurred. The photo-oxidation of run 4 ($[H_2O_2]_0/[PhCO_2H]_0$ 8.9) exhibited the same tendency as run 2a and the decomposition of H_2O_2 was 19% and that of $PhCO_2H$ was 67% after 10 h irradiation. This inhibition of reaction may be due to the formation of polyhydroxylated aromatics and/or polymer which absorbs the light. However, in run 5a ($[H_2O_2]_0/[PhCO_2H]_0$ 24.6), the solution turned yellow after 2 h and then colourless again after 9 h, when $PhCO_2H$ was completely decomposed. On the other hand, the decomposition of H_2O_2 proceeded smoothly after disappearance of the colour.

In the case of run 6 ($[H_2O_2]_0/[PhCO_2H]_0$ 100), $PhCO_2H$ was completely decomposed after 6 h and finally, CO_2 evolved from $PhCO_2H$ decomposed (1.8M) was 11.0M, suggesting the necessity of a large excess (*ca.* 25 fold) of H_2O_2 for the complete oxidation of $PhCO_2H$.

On the other hand, the efficiency of H_2O_2 for decomposing $PhCO_2H$, *i.e.*, [decomposed $PhCO_2H$]/[decomposed H_2O_2], is 0.63 for run 2a, 0.38 for run 4, and 0.34 for run 5a at 6 h. This suggests that at higher concentration of H_2O_2 (*e.g.*, run 5a), H_2O_2 (or HO•) is consumed in the further reaction stage together with the initial stage of oxidation of $PhCO_2H$, *i.e.*, additional H_2O_2 or HO• is consumed in nonbenzoic acid reactions.

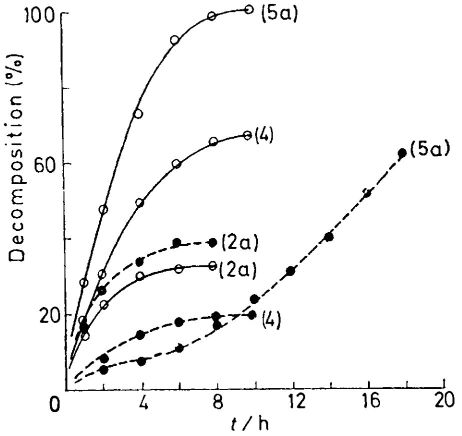


FIGURE 1 Decomposition of $PhCO_2H$ and H_2O_2. $[PhCO_2H]_0$ 2.15×10^{-2}M. $[H_2O_2]_0$ 0.28×10^{-1}M for (2a), 1.91×10^{-1}M for (4), and 5.30×10^{-1}M for (5a). Solid lines represent the decomposition of $PhCO_2H$ and broken lines represent the decomposition of H_2O_2

Products.—In the photo-oxidation of $PhCO_2H$ (1.72×10^{-2}M) with H_2O_2 (4.22×10^{-1}M) ($[H_2O_2]_0/[PhCO_2H]_0$ 24.5), hydroxybenzoic acids, phenol, benzene, and CO_2 were obtained as primary products.

With the progress of decomposition of H_2O_2, the yields of primary products except CO_2 decrease, while aliphatic acids appear. These acids, *e.g.*, $HO_2CCH{=}CHCO_2H$, $HO_2CCH_2CO_2H$, $HOCH_2CO_2H$, HO_2CCO_2H, CH_3CO_2H, and HCO_2H, *etc.*, are detected by g.c.–m.s. and g.l.c. Furthermore, phenylbenzoic acids ($PhC_6H_4CO_2H$), dihydroxybenzenes (HOC_6H_4OH), and muconic acid ($HO_2CCH{=}CH{-}CH{=}CHCO_2H$) were detected. All these products were obtained as their esters from methylation using diazomethane.

$$PhCO_2H \xrightarrow{h\nu} PhH + CO_2 \qquad (5)$$

$$PhCO_2H \xrightarrow{h\nu} PhOH + CO \qquad (6)$$

Figure 2 shows the time dependence of the evolution of CO_2 and Figure 3 that of the yields of other liquid products. Figure 2 shows that the evolution of CO_2 is much lower than $PhCO_2H$ decomposed at the initial stage of the photo-oxidation (<5 h), but after decomposition of a considerable amount of $PhCO_2H$ the evolution of CO_2 increased rapidly and this tendency correlates with the decomposition of H_2O_2. This low yield of CO_2 at the initial stage suggests that equations (5) and (6) are less important pathways for the decomposition of $PhCO_2H$, but they are major paths in gas-phase photolysis.[6] That equations (5) and (6) are minor pathways is also indicated by the control run 1, where no decomposition of $PhCO_2H$ occurred in the absence of H_2O_2. Carbon monoxide from equation (6) should be oxidised quickly under these conditions to CO_2.

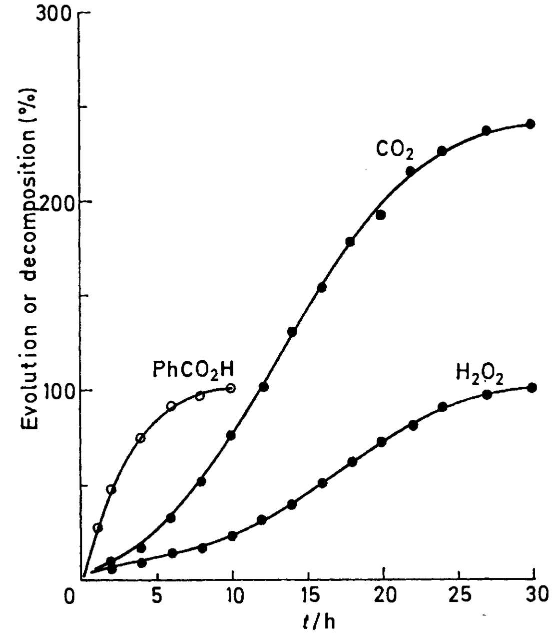


FIGURE 2 Evolution of CO_2 and decomposition of $PhCO_2H$ and H_2O_2. $[PhCO_2H]_0$ 1.72×10^{-2}M, $[H_2O_2]_0$ 4.22×10^{-1}M($[H_2O_2]_0/[PhCO_2H]_0$ 24.5)

Figures 2 and 3 show that the total yield of products at 10 h was *ca.* 50% and that at 16 h was 66% for 100% decomposition of $PhCO_2H$. The low yield may be due to the escape of gaseous products during condensation

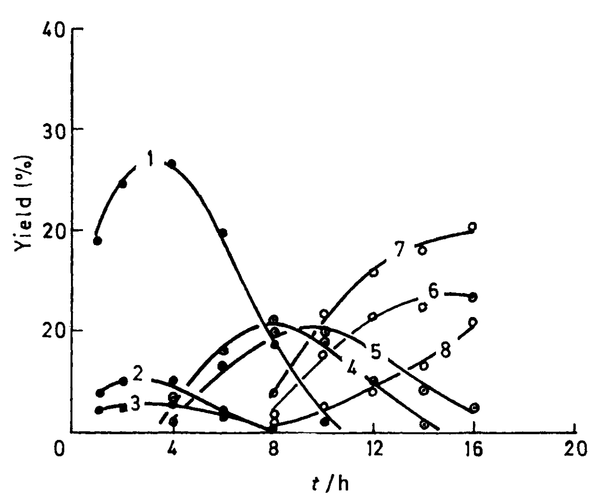
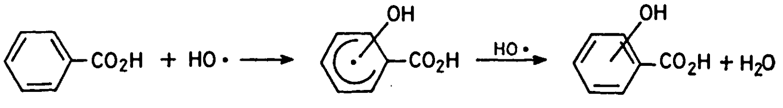


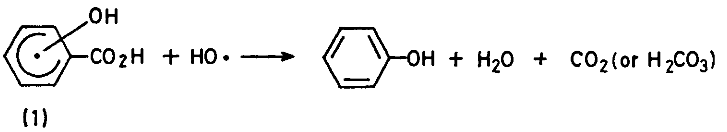
FIGURE 3 Time dependence of product yields. $[PhCO_2H]_0$ 1.72×10^{-2}M, $[H_2O_2]_0$ 4.22×10^{-1}M ($[H_2O_2]_0/[PhCO_2H]_0$ 24.5). Yield (%) = 100 [(carbon numbers of product)/(carbon number of substrate)] × ([product]/[$PhCO_2H$ decomposed]). 1, $HOC_6H_4CO_2H$; 2, PhOH; 3, PhH; 4, $HO_2CCH{=}CHCO_2H$; 5, $HO_2CCH_2CO_2H$; 6, $HO_2C{\cdot}CO_2H$; 7, CH_3CO_2H; 8, HCO_2H

and/or esterification work-up and also to the formation of unestimated muconic acid and unidentified products (M^+ 206, 222, 240, and 256).

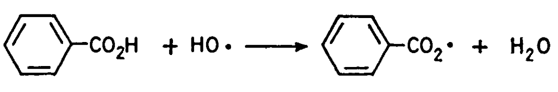
Mechanism.—The oxidation of $PhCO_2H$ should start from the addition of HO• to the aromatic ring to give hydroxybenzoic acid [equation (7)], since the contribution of equations (5) and (6) giving PhH and PhOH is negligible, in view of no occurrence of decomposition of $PhCO_2H$ in the absence of H_2O_2. Therefore, alternative pathways for the formation of PhH and PhOH are necessary [equations (8)—(11)]. Evidence for the existence of (2) and (3) is given by the detection of $PhCO_2C_6H_4CO_2H$ and $PhC_6H_4CO_2H$, respectively, which were identified by g.l.c.–m.s.


(1)

(7)


(1)

(8)


(2)

(9)

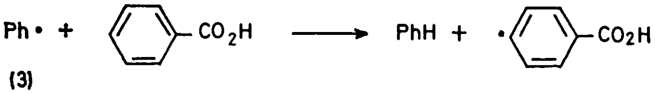

(2) (3)

(10)

$$\underset{(3)}{Ph\cdot} + HO\cdot \longrightarrow PhOH \qquad (11)$$

The yield of PhOH in a quartz vessel was about twice that in a Pyrex vessel. This may be due to radical coupling [equation (11)], because the concentration of HO• in a quartz vessel is higher than that in a Pyrex vessel, *i.e.*, the decomposition rate of H_2O_2 in a quartz vessel is higher than that in a Pyrex vessel, as stated above.

Phenyl radical (3), generated as in equations (9) and (10), may abstract hydrogen atom to form benzene [equations (12)[12] and (13)]. Under the experimental conditions, equation (13) would be a major path for the formation of PhH, since H_2O_2 is in large excess and hydrogen atom abstraction from the ring [equation (12)] is energetically unfavourable. The primary products thus formed are further oxidised to give C–C cleavage products of the ring. The detection of muconic acid by g.l.c.–m.s. shows that pathways similar to the oxidation of catechol by peracetic acid [8-10] may exist in this photo-oxidation (Scheme). It is known that tricarboxylic acid (4) evolves CO_2 upon u.v. irradiation,[5] and α-keto-carboxylic acid (5), which may be formed from 2,3-dihydroxybenzoic acid or its quinone similar to enzyme-catalysed oxidation of 2,3-dihydroxybenzoate,[13] may react with H_2O_2 to evolve CO_2 by analogy with pyruvic acid (CH_3COCO_2H), which reacts with H_2O_2 immediately to give acetic acid and CO_2.[14]

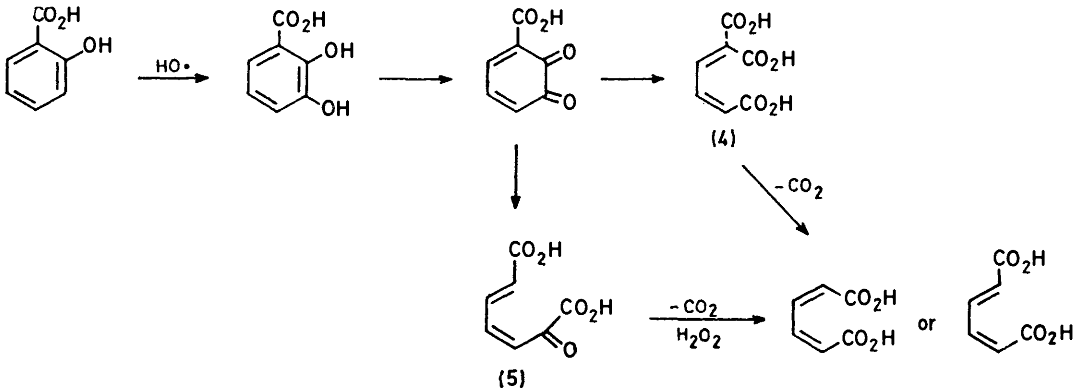

(3)

(12)

$$\underset{(3)}{Ph\bullet} + HOO{-}H \longrightarrow PhH + HOO\bullet \qquad (13)$$

Lower aliphatic acids may be formed *via* polyhydroxylation of benzoic acid followed by ring rupture, rather than *via* muconic acid, since the yield of muconic acid is low. Dicarboxylic acids with five or seven carbons were not detected, probably because they would be formed *via* α-keto-carboxylic acids which decarboxylate to acids having four or six carbons. Polyhydroxylated acids, which should be formed in this oxidation, were not detected by g.l.c.–m.s., probably because such compounds may be further oxidised by HO• and/or HOO•.

In summary, in this photo-oxidation of $PhCO_2H$, the decomposition of $PhCO_2H$ and H_2O_2 stops at the stage of polyhydroxylation of aromatics or polymer, if $[H_2O_2]_0/[PhCO_2H]_0 < 10$, but at $[H_2O_2]_0/[PhCO_2H]_0 \gtrsim 25$, $PhCO_2H$ is oxidised to aliphatic acids, and at $[H_2O_2]_0/[PhCO_2H]_0 > 100$, $PhCO_2H$ may be completely oxidised to CO_2 and H_2O. The cleavage of the aromatic ring may occur after di- or poly-hydroxylation, and decarboxylation from $PhCO_2H$ [equations (9) and (10)] is a probable pathway for formation of PhH and PhOH.



SCHEME

EXPERIMENTAL

Benzoic acid was purified by recrystallisation from water (m.p. 122 °C) and 90% hydrogen peroxide was purchased from Mitsubishi Gas Chem. Co. and estimated iodometrically; the independent analyses of H_2O_2 and peracid were done according to Swern's method.[11] Diazomethane–ether solution was prepared by the method of Arndt.[15,16]

G.l.c. analyses were performed on a model G 180 Yanagimoto gas chromatograph with flame ionisation and thermal conductivity detectors. A Shimadzu g.l.c.–m.s. 7000 gas chromatograph–mass spectrometer was used to identify and estimate photo-oxidation products. A Halos high-pressure 300 W mercury lamp was used as a light source. All experiments were carried out in a 1 l vessel with quartz or Pyrex filter or in a cylindrical quartz or Pyrex vessel (2 × 12 cm) with a water jacket.

G.l.c.–m.s. analysis of photo-oxidation products

Compound	M^+	m/e (main values)					
HCO_2Me	60	45	44	29	28		
CH_3CO_2Me	74	45	43	31	29	28	
$HOCH_2CO_2Me$	90	59	44	31	29	28	
MeO_2CCO_2Me	(118) [a]	87	59	31			
$MeO_2CCH_2CO_2Me$	(132) [a]	101	74	59	57	43	29
$MeO_2CCH{=}CHCO_2Me$	(144) [a]	113	112	85	59	31	
$MeO_2CCH{=}CH{-}CH{=}CHCO_2Me$	(170) [a]	139	138	111	59	31	
PhOH	94	66	65				
$HOC_6H_4CO_2Me$	152	121	120	93	65	43	39
HOC_6H_4OH	110	92	82	81	64		
$PhC_6H_4CO_2Me$	212	181	153	59	31		
$PhCO_2C_6H_4CO_2Me$	256	225	197	121	59	31	

[a] No M^+ was detected.

Products.—The gaseous products evolved by photo-oxidation were collected in a gas burette (300 ml) connected with a capillary tube to the reaction vessel. Concentration of CO_2 in the gas was measured by the volume absorbed in 33% aqueous KOH,[17] and analysis of O_2 was done by measurement with an alkaline pyrogallol solution,[17] where the yield of O_2 increased as the concentration of H_2O_2 increased.

To remove unchanged H_2O_2 remaining in solution, $Na_2S_2O_3$ (powder) was added to the solution under cooling (*ca.* 0 °C) and the solution was concentrated under reduced pressure below 20 °C. To the concentrate, (i) a mixture of MeOH and Et_2O was added and then (ii) a diazomethane–ether solution was added to esterify carboxylic acids.

The solutions [(i) and (ii)] including products were analysed by g.l.c. and g.l.c.–m.s. using two columns (PEG 20M Chromosorb W and Silicone OV 17). The Table shows the mass spectra of products. Analysis of CO_2 was done by acidimetry of aqueous $Ba(OH)_2$.

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REFERENCES

[1] L. Kaplan, L. A. Wendling, and K. E. Wilzbach, *J. Amer. Chem. Soc.*, 1971, **93**, 3819.

[2] L. Kaplan, L. A. Wendling, and K. E. Wilzbach, *J. Amer. Chem. Soc.*, 1971, **93**, 3821.

[3] K. Omura and T. Matsuura, *Tetrahedron*, 1969, **24**, 3475.

[4] C. R. E. Jefcoate, J. R. L. Smith, and R. O. C. Norman, *J. Chem. Soc.* (*B*), 1969, 1013.

[5] M. Mousseron-Canet and J. C. Mani, 'Photochemistry and Molecular Reactions,' Israel Program for Scientific Translation Ltd., 1972, pp. 69—70.

[6] F. Chau, C. Gibbons, and D. Barton, *Canad. J. Chem.*, 1972, **50**, 2017.

[7] J. K. Kochi, 'Free Radicals,' Wiley, New York, 1973, vol. 1, pp. 80—83.

[8] J. Böeseken, *Proc. Akad. Soc. Amsterdam*, 1932, **35**, 750 (*Chem. Abs.*, 1933, **27**, 1332).

[9] J. Böeseken and C. L. M. Kerkhoven, *Rec. Trav. chim.*, 1932, **51**, 964 (*Chem. Abs.*, 1933, **27**, 2938).

[10] A. J. Pandell, *J. Org. Chem.*, 1976, **41**, 3992.

[11] D. Swern, 'Organic Peroxides,' Wiley–Interscience, 1970, p. 501.

[12] H. G. C. Bates, M. G. Evans, and N. Uri, *Nature*, 1950, **166**, 869.

[13] S. Dagley and D. A. Stopher, *Biochem. J.*, 1959, **73**, 16.

[14] Y. Ogata, K. Tomizawa, and K. Takagi, to be published.

[15] F. Arndt, *Org. Synth.*, 1950, Coll. Vol. 2, 165.

[16] F. Arndt, *Org. Synth.*, 1950, Coll. Vol. 2, 461.

[17] K. Hata, N. Sugiyama, T. Kobayashi, M. Ohta, and M. Ohki, 'Kagaku Zikken-Hoh,' Tokyo Kagaku Dozin, Tokyo, 1974, pp. 348—349.