# Photoreaction of Benzoic Acid with Sodium Hypochlorite in Aqueous Alkali

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The photoreaction of benzoic acid with sodium hypochlorite in aqueous alkali (pH $\geqslant$ 12) has been studied. At a low initial ratio of $[ClO^-]/[PhCOO^-]$, *e.g.* 0.1, hydroxylation and chlorination at the aromatic ring occur simultaneously with *ipso*-substitution of the carboxylate group to give hydroxy- and chlorobenzoic acids together with phenol. The product distribution depends on the wavelength of light, which implies the dependence on the concentration of active species generated from $ClO^-$ and on the light stability of products. At comparable concentrations of $ClO^-$ and $PhCOO^-$, the products initially formed from the photoreaction react further with $ClO^-$ in the dark to give polychlorinated derivatives. The initial steps for the photoreaction are discussed on the basis of the reactivity of the active species, $O(^3P)$, $O(^1D)$, $O^{-\cdot}$, and Cl·, generated by photolysis of $ClO^-$.

Sodium hypochlorite can be used for selective oxidation and halogenation of organic compounds,[1] and for oxidative removal of pollutants.[2] Hypochlorite ion ($ClO^-$) under irradiation delivers highly active atomic oxygen, $O(^3P)$ and $O(^1D)$, along with $O^{-\cdot}$ depending on the wavelength used.[3,4] The gas-phase reactions of $O(^3P)$ were reported.[5]

As we have reported,[6a] the reaction of benzoic acid with HO· radical from irradiated $H_2O_2$ under acidic conditions is mainly initiated by addition of HO· to the ring and by hydrogen atom abstraction from COOH as a minor process [equation (1a)].[6a] On the other hand, in the reaction of $PhCOO^-$ with HO· under neutral conditions, *ipso*-attack of HO· on $PhCOO^-$ [equation (1b)] together with addition of HO· to the ring are observed.[6b]

$$PhCOOH + HO\cdot \xrightarrow{-H_2O} PhCOO\cdot \longrightarrow Ph\cdot + CO_2 \qquad (1a)$$

$$PhCOO^- + HO\cdot \longrightarrow Ph(OH)COO^{-\cdot} \xrightarrow{-H} PhOH + CO_2 \qquad (1b)$$

The present study reports that the title reaction leads preferentially to hydroxylation rather than chlorination. The reaction mechanism is discussed.

## Results and Discussion

For an examination of the dependence of the reactivity of active species on the wavelength, a mixture of PhCOONa (0.01M) and NaClO (0.001—0.200M) in aqueous alkali (pH $\geqslant$ 12) was photolysed at 254 and >350 nm. The remaining $ClO^-$ after irradiation was quickly reduced with aqueous $Na_2S_2O_3$. The reaction products observed by g.l.c. and g.l.c.–mass spectrometry were composed of hydroxybenzoic acids ($p \gtrsim o > m$), chlorobenzoic acids ($o \gtrsim p > m$), phenol, and chlorophenols.

The decomposed percentage of benzoic acid with $ClO^-$ decomposed and the product yields based on the decomposed benzoic acid are listed in Table 1, where the yields of hydroxybenzoic acids and phenol include those of their chlorinated compounds. Both hydroxybenzoic acids and phenol react rapidly with $ClO^-$ in the dark to give their chloro-derivatives.

As shown in Table 1, the conversion of $PhCOO^-$ based on decomposed $ClO^-$, *i.e.* the ability of $ClO^-$ to decompose $PhCOO^-$, is high when the ratio of $[ClO^-]_0/[PhCOO^-]_0$ is low, *e.g.*, at $[ClO^-]_0/[PhCOO^-]_0 = 0.01$, the efficiency for the decomposition of $PhCOO^-$ is 42% at 254 nm and 37% at >350 nm, while at $[ClO^-]_0/[PhCOO^-]_0$ 1.0, 24% at 254 nm and 19% at >350 nm. This decrease of efficiency at the higher ratio of 1.0 may be ascribed to the consumption of $ClO^-$ by the spontaneous decomposition of $ClO^-$ induced by active species such as atomic O, Cl, and organic radicals before reacting with $PhCOO^-$.

The time dependence of product yield at $[ClO^-]_0/[PhCOO^-]_0$ 0.1 is shown in Table 3. The decomposition ratio of $PhCOO^-$ *versus* $ClO^-$ decreased with increasing irradiation time, *i.e.* $ClO^-$ is photodecomposed spontaneously and by the reaction with $PhCOO^-$; it can also react with hydroxylated products in the dark. Hence, as the reaction proceeds, the yield of hydroxybenzoic acid decreases, while that of chlorohydroxybenzoic acid increases, especially by >350 nm irradiation. The yield of chlorinated compounds at 254

**Table 1.** Product yields of photoreaction of PhCOOH with NaClO in aqueous alkali (pH $\geqslant$ 12) at 20—21 °C [a]

| | | | Product yield (%) [d] | | | |
|---|---|---|---|---|---|---|
| Ratio [b] | λ/nm | PhCOOH decomposed (%) [c] | $HOC_6H_4COOH$ | $ClC_6H_4COOH$ | PhOH | Others |
| 0.1 | 254 | 42.3 | 60 (5) | ~1 | <1 | |
| 0.5 | 254 | 30.2 | 64 (23) | 1 | 1 (1) | |
| 1.0 | 254 | 24.1 | 42 (37) | 3 | 2 (2) | *e* |
| 0.1 | >350 | 36.8 | 71 (31) | 5 | 5 (4) | *e* |
| 0.5 | >350 | 27.3 | 65 (41) | 5 | 7 (7) | *e* |
| 1.0 | >350 | 19.1 | 64 (58) | 4 | 6 (6) | *e* |

[a] Initial concentration of benzoic acid $[PhCOOH]_0$ was 0.01M. Irradiation time: 120 min at 254 nm, 40 min at >350 nm [b] $[ClO^-]/[PhCOO^-]_0$. [c] Based on $ClO^-$ decomposed. [d] Based on PhCOOH decomposed: the parentheses indicate chlorinated compound derived from the dark reaction with $ClO^-$. [e] Dichloro-derivatives were detected by g.l.c.

nm was lower than that at >350 nm, which may be explained by secondary photolysis, *i.e.* chlorinated aromatic compounds are decomposed in aqueous alkali alone by absorbing the 254 nm irradiation, but they are stable to light of wavelength >350 nm which is not absorbed. For example, chlorohydroxybenzoic acids were *ca.* 50% decomposed by 2 h irradiation at 254 nm; this photolysis was accelerated in the presence of $PhCOO^-$. On the other hand, no photolysis was observed at >350 nm. Both chlorobenzoic acids and chlorophenols in aqueous alkali were decomposed by 254 nm light, *e.g.*, *ca.* 30% for chlorobenzoic acid and 10% for chlorophenol for 2 h irradiation. These percentages are lower than that of chlorohydroxybenzoic acid.

The yields of chlorinated products increase as the concentration of $ClO^-$ increases (Table 1); this trend is explicable by the easy chlorination of hydroxylated aromatic compounds with $ClO^-$ in the dark.

Benzene and phenylbenzoic acid were other products detected. Also the presence of $CO_2$ was confirmed by the $Ba(OH)_2$ test. At high ratio of $[ClO^-]_0/[PhCOO^-]_0$, *e.g.*, over 20, $PhCOO^-$ was completely decomposed to give $CO_2$ together with acetic and oxalic acids and unknown products. The Figure shows the percentage formation of $CO_2$ from $PhCOO^-$ decomposed. The formation of $CO_2$ was observed even at the initial stage. Hence $CO_2$ is formed not only *via* complete oxidation, but also *via* substitution of the carboxylate group by radicals or an electron transfer from $PhCOO^-$ to radicals.

*Mechanism of Initial Stage*.—Benzoate ion has $\lambda_{max.}$ at 224 nm (ε 8 350) and $ClO^-$ has $\lambda_{max.}$ at 292 nm (ε 390). The 254 nm light is absorbed by both $PhCOO^-$ and $ClO^-$, while the >350 nm light is absorbed only by $ClO^-$ because there is no u.v. absorption of $PhCOO^-$ at >300 nm

**Table 2.** Isomeric distribution of dark reaction products of hydroxylated compounds with $ClO^-$ in aqueous alkali (pH $\geqslant$ 12) at 20 °C [a]

| Hydroxylated compound | Yield (%) [b] | Isomeric distribution |
|---|---|---|
| $2\text{-}HOC_6H_4COOH$ | 87 | $3\text{-}Cl\text{-}2\text{-}HOC_6H_3COOH$ (40),<br>$5\text{-}Cl\text{-}2\text{-}HOC_6H_3COOH$ (60) |
| $3\text{-}HOC_6H_4COOH$ | 82 | $2\text{-}Cl\text{-}3\text{-}HOC_6H_3COOH$ (4),<br>$4\text{-}Cl\text{-}3\text{-}HOC_6H_3COOH$ (46),<br>$6\text{-}Cl\text{-}3\text{-}HOC_6H_3COOH$ (44) |
| $4\text{-}HOC_6H_4COOH$ | 89 | $3\text{-}Cl\text{-}4\text{-}HOC_6H_3COOH$ (85),<br>$3,5\text{-}Cl_2\text{-}4\text{-}HOC_6H_2COOH$ (15) |
| PhOH | 93 | $2\text{-}ClC_6H_4OH$ (80),<br>$4\text{-}ClC_6H_4OH$ (20) |

[a] Initial concentration of hydroxy compound and $ClO^-$ : 0.1M. Reaction time: 1 h for 3-, 4-hydroxybenzoic acids and phenol; 2.5 h for 2-hydroxybenzoic acid. [b] Based on $ClO^-$ decomposed.

Active species generated on photolysis of aqueous NaClO were reported to be $O(^3P)$, $O^{-\cdot}$, $O(^1D)$, $Cl\cdot$, and $HO\cdot$, the last one being derived from the reaction of water with $O(^1D)$ and $O^{-\cdot}$.[4,5] For a basic solution of pH 12, *ca.* 50% of $HO\cdot$ would be present as $O^{-\cdot}$ because the $pK_a$ of $HO\cdot$ is 11.9.[7] Atomic chlorine is less reactive and has a longer life than atomic oxygen of $HO\cdot$.[8]

The quantum yields for three types of photodecomposition of $ClO^-$ [equation (2)] are $\varphi_a$ 0.08, $\varphi_b$ 0.278, and $\varphi_c$ 0.133 at 254 nm and $\varphi_a$ 0.28 and $\varphi_b$ 0.08 at 365 nm in aqueous alkali.[4] Hence the 254 nm photolysis of $ClO^-$ should generate

$$ClO^- \xrightarrow{h\nu} \begin{cases} Cl^- + O(^3P) \quad \varphi_a & (2a) \\ Cl\cdot + O^{-\cdot} \quad \varphi_b & (2b) \\ Cl^- + O(^1D) \quad \varphi_c & (2c) \end{cases}$$

$O(^3P)$, $O^{-\cdot}$, $O(^1D)$, and $Cl\cdot$ as active species, while >350 nm photolysis should give $O(^3P)$, $O^{-\cdot}$, and $Cl\cdot$, but no $O(^1D)$, although the distribution of active species may be different from that reported by Buxton.[4] The concentration of $Cl\cdot$ at 254 nm (φ 0.278) must be higher than that at >350 nm (φ 0.08) based on the available quantum yield.[4]

Chlorobenzoic acid may be a primary product formed directly by the addition of atomic chlorine whereas chloro-

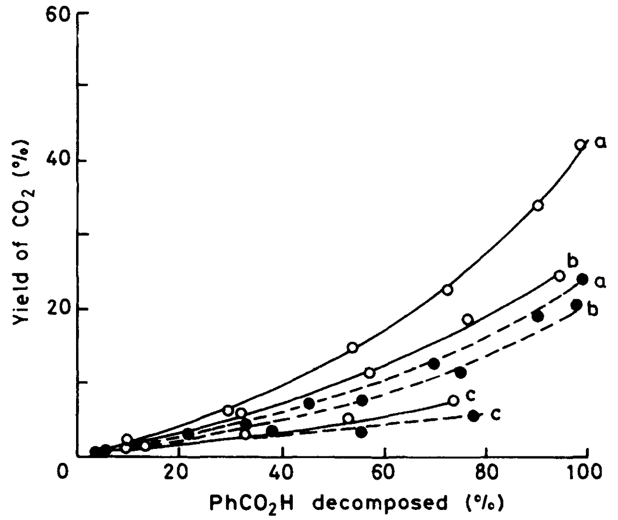
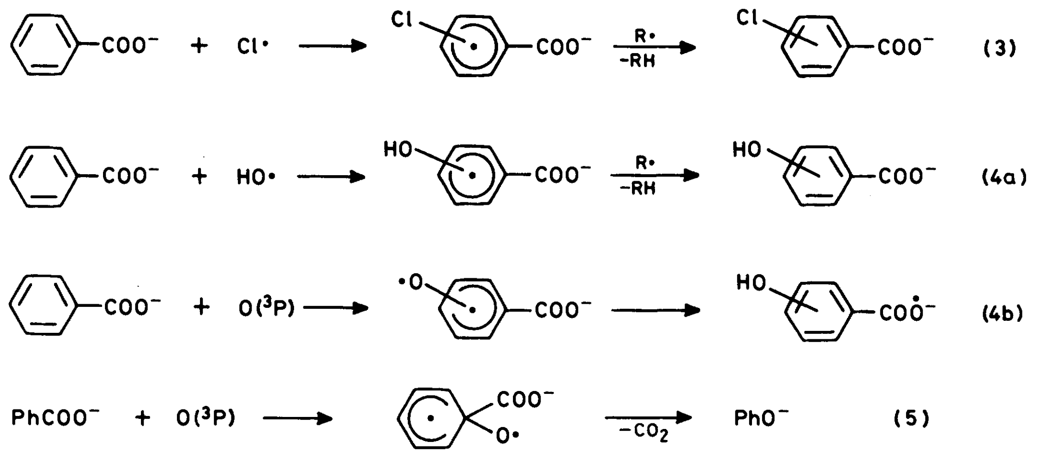


**Figure.** Plots of yield of $CO_2$ *versus* percentage of decomposed PhCOOH at various ratios of $[ClO^-]_0/[PhCOO^-]_0$ for the photoreaction of $PhCOO^-$ with $ClO^-$. Yield (%) of $CO_2$ was calculated on the basis of the stoicheiometry: $PhCOOH \longrightarrow 7\ CO_2$. (○) 254 nm light irradiation; (●) >350 nm light irradiation. $[ClO^-]_0/[PhCOO^-]_0$ 25 (curve a), 20 (curve b), 10 (curve c)

**Table 3.** Time dependence of product yields of photoreaction of PhCOOH with NaClO in aqueous alkali (pH $\geqslant$ 12) [a]

| λ/nm | *t*/min | $ClO^-$ decomposed (%) | $10^2PhCOOH$ decomposed (mmol) | Product yield (%) [b] | | |
|---|---|---|---|---|---|---|
| | | | | $HOC_6H_4COOH$ | $ClC_6H_4COOH$ | PhOH |
| 254 | 30 | 21 | 3.04 | 64 (3) | 3 | 2 (1) |
| 254 | 60 | 38 | 5.22 | 65 (2) | 1 | 2 (2) |
| 254 | 120 | 71 | 7.40 | 60 (5) | ~1 | <1 |
| >350 | 10 | 28 | 3.38 | 78 (24) | 5 | 6 (4) |
| >350 | 20 | 54 | 5.29 | 74 (29) | 6 | 6 (5) |
| >350 | 40 | 92 | 7.20 | 71 (31) | 5 | 5 (4) |

[a] $[ClO^-]_0/[PhCOO^-]_0$ 0.1, $[PhCOO^-]_0$ 0.01M, volume of the solution is 200 ml. [b] Based on PhCOOH decomposed. Parentheses indicate chlorinated compounds derived from the dark reaction with $ClO^-$.



$$PhCOO^- + HO\cdot(\text{or } Cl\cdot) \longrightarrow PhCOO\cdot + HO^- (\text{or } Cl^-) \qquad (6a)$$

$$PhCOO\cdot \xrightarrow[-CO_2]{} Ph\cdot \xrightarrow[\text{Coupling}]{HO\cdot} PhOH \qquad (6b)$$

hydroxybenzoic acids and chlorophenols would be formed *via* the dark reaction of ring-hydroxylated compounds with NaOCl.

Hydroxybenzoic acids may be formed *via* addition of HO• or O($^3$P) to the aromatic ring followed by a hydrogen atom abstraction [equation (4)] in a manner similar to chlorination [equation (3)], where R• is any radical.

Since the quantum yield for the formation of Cl• ($\varphi_b$ 0.278) is smaller than that of HO• ($\varphi_b + \varphi_c$ 0.411) as shown in equation (2), the yield of chlorobenzoic acid at 254 nm is much lower than that of hydroxybenzoic acids even if the direct photolysis of chlorobenzoic acid is taken into account. The lower yield of chlorobenzoic acid may also be ascribed to the lower reactivity of Cl• than those of HO• or O($^3$P),[8] because hydrogen abstraction and addition to the aromatic ring are similar in that the driving force for both reactions is pairing of odd electrons. Probably, Cl• may mainly act as a hydrogen atom abstractor R• from the adducts [equations (3) and (4)], but does not add to the aromatic ring.

Two pathways are probable for the formation of phenol: (a) *ipso*-attack of O($^3$P),[5b] but not HO•,[6b] on the ring carbon bearing COO$^-$ [equation (5)] as reported for the reaction of toluene with O($^3$P)[5b] and (b) electron transfer of PhCOO$^-$ to radicals followed by decarboxylation and coupling with HO• [equation (6)].

The fact that the yield of phenol at >350 nm is higher than at 254 nm even at the initial stage of the photolysis agrees with the higher concentration of O($^3$P) at >350 nm than at 254 nm.[4] Hence O($^3$P) contributes largely to the formation of phenol. The formation of traces of phenylbenzoic acid and benzene implies the formation of phenyl radical as an intermediate. Since there is no direct photodecarboxylation, an electron transfer from PhCOO$^-$ to HO• and/or Cl• is conceivable. Unfortunately, the control runs for this electron transfer failed in a photoreaction of PhCOO$^-$ with $H_2O_2$ or $Cl_2$ because of the rapid and spontaneous decomposition of $H_2O_2$ even in the dark and also the rapid conversion of $Cl_2$ into ClO$^-$ in aqueous alkali of pH 12.

Since the yield of phenol parallels with the generation of O($^3$P) at various wavelengths and since traces of phenylbenzoic acid and benzene are formed, phenol may be formed *via* equations (5) and (6), *i.e.* *ipso*-attack of O($^3$P) on the COO$^-$ group and one-electron transfer, the former being the main path for phenol formation.

Primary products thus formed, *i.e.* hydroxy- and chlorobenzoic acids and phenol, undergo further reactions with ClO$^-$ in the dark, direct photolysis, and/or reactions with active species formed from ClO$^-$ under irradiation, giving various products.

As shown in the Figure, the yield of $CO_2$ at a high ratio of $[ClO^-]_0/[PhCOO^-]_0$, *e.g.* 20, increases with the time of irradiation. As stated before, highly oxidised products, *e.g.* polyhydroxylated products, may be oxidised with evolution of $CO_2$ to degradation products and finally to acetic and oxalic acids, *etc.*

## Experimental

*Materials.*—Aqueous NaClO (*ca.* 1M) was prepared by introducing gaseous $Cl_2$ into aqueous NaOH (2.1M) at 0 °C and the concentration of ClO$^-$ was determined by iodometry. Benzoic acid was purified by recrystallisation from water, m.p. 121—122 °C. *o*- and *p*-chlorobenzoic acid were prepared by the $KMnO_4$ oxidation of the corresponding chlorotoluenes, m.p. 141—142 °C for the *ortho*- and 241—243 °C for the *para*-isomer.[9] Other reagents were of guaranteed grade.

*Apparatus.*—U.v. spectra were recorded of a Hitachi 124 spectrophotometer. M.p.s were measured by a Yanagimoto micro m.p. apparatus. pH was measured by a Hitachi–Horiba M7 pH meter. G.l.c. analyses were performed on a Yanagimoto G 180 gas chromatograph with flame ionisation detector using three sorts of columns (PEG 20M, KG-02, and Bentone 34). G.l.c.–mass spectral analyses were conducted with a JEOL LMS D-300 mass spectrometer. The measurement of the fluorescence of PhCOO$^-$ was done by a Hitachi 650-10S fluorescence spectrophotometer. A Halos low-pressure 60 W Hg lamp and a Phillips super-pressure 500 W Hg lamp were used as light sources.

*Photoreaction of Benzoate Ion with Hypochlorite Ion.*—A mixture of benzoic acid (0.01M) and sodium hypochlorite (0.001—0.200M) in aqueous NaOH (200 ml; pH $\gtrsim$ 12) under nitrogen was irradiated using a Halos low-pressure 60 W

Hg lamp through a quartz filter in a quartz cell (254 nm irradiation) or a Phillips super-pressure 500 W Hg lamp through a naphthalene filter (50 mm; 0.5M) in a Pyrex cell (>350 nm irradiation). The concentration of $ClO^-$ was measured by iodometry.

Unchanged $ClO^-$ in a 10 ml portion was quickly decomposed by adding excess of aqueous $2M-Na_2S_2O_3$ and the solution was then acidified with aqueous $H_2SO_4$. This work-up suppressed the further oxidation of hydroxylated products and the evolution of $Cl_2$ on acidification. The solution thus treated was extracted with ether (3 × 20 ml), dried ($Na_2SO_4$), and esterified by ethereal diazomethane. The reaction products were estimated and identified by g.l.c. and g.l.c.–mass spectral comparison with authentic samples. Another portion was acidified and $CO_2$ was expelled by $N_2$ bubbling and estimated by absorption in aqueous $Ba(OH)_2$ followed by acidimetry with aqueous HCl.

*Dark Reaction.*—*o*-, *m*-, and *p*-hydroxybenzoic acids and phenol (0.01M) in aqueous alkali were oxidised by $ClO^-$ (0.01M) within 1 h except for *o*-hydroxybenzoic acid. Work-up and identification were similar to those described in the photoreaction and products were identified by g.l.c. and g.l.c.–mass spectroscopy. Oxidation products and yields are shown in Table 2.

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