Photochemical Nitration of Benzoic Acid Derivatives by Irradiation to Nitrate Ions

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Synopsis. Photochemical nitration of *p*-hydroxybenzoate, HBA, initiated by UV irradiation to sodium nitrate or sodium nitrite was observed in aqueous solutions. 4-Hydroxy-3-nitrobenzoate was formed, with maximum quantum yields of 0.007 and 0.09 for $NaNO_3$ and $NaNO_2$, respectively. From the dependence of the yields on the pH and concentrations of oxygen and OH-scavengers, we propose a mechanism involving the addition of OH· to the aromatic ring of HBA and electron abstraction from NO_2 by the OH· adduct for the photonitration.

Nitrate ion is a source of hydroxyl radical (the protonated form of O^{-}·) and atomic oxygen in photodissociations by UV-light. There is, however, no net-reaction of nitrate ion in the absence of a substrate, since photodissociation products usually remain in a solvent cage and recombine very rapidly.[1-4]

It has been observed that photoexcitation of nitrate ion in aqueous solutions induces hydroxylation of dissolved organic substrates; phenol, chlorophenols, and nitrophenols are converted mainly into benzenedioles, chlorobenzenedioles, and nitrobenzenedioles, respectively, without noticeable nitration of the substrates.[5-7] When a substrate with high reactivity to both NO_2 and OH· is present by irradiation, nitrate ion could also induce the formation of nitro derivatives which are occasionally mutagenic compounds.[8] It was reported that photochemical nitration of butyl 4-hydroxybenzoate occurred by irradiation of nitrite ion at 366 nm to generate a mutagenic compound, butyl 4-hydroxy-3-nitrobenzoate, in aerated aqueous solutions.[9,10] Further, it was confirmed that NO is oxidized to NO_2 by dissolved oxgyen, and the two radicals OH· and NO_2 are involved in the photonitration. In the case of NO_3^- irradiation, the OH· and NO_2 radicals appear to be simultaneously produced at pH<12 to result in photonitration. The purpose of the present work is to identify the photoproducts and to investigate the mechanism of the photonitration by excitation of nitrate ion in the presence of benzoic acid and phenol derivatives as substrates.

Experimental

Materials. Derivatives of benzoic acid and phenol (Tokyo Kasei, G. R.), and sodium nitrite and sodium nitrate (Kanto Kagaku, G. R.) were used as received. The pH was adjusted with sodium hydroxide. Freshly redistilled water was used as solvent.

Procedures. A sample in a cell (1×1×4 cm) was irradiated at 25°C in a steady-light illumination apparatus with a 400 W high pressure Hg lamp at λ=313 nm, using a UV cold-mirror and cut-off filter (Kenko, U340). The light intensity was measured by potassium trioxalato ferrate(III) actinometry (I_0=1.8×10^{-8} mol cm^{-2} s^{-1}). The quantum yields for the 4-hydroxybenzoate (HBA) disappearance, Φ_{-HBA} and the 4-hydroxy-3-nitrobenzoate (HNB) formation, Φ_{HNB} were determined by the equations $-\Delta[HBA]/\Delta t=\Phi_{-HBA}I_{ab}$ and $\Delta[HNB]/\Delta t=\Phi_{HNB}I_{ab}$, where I_{ab} is the quantitiy of photons absorbed by $NaNO_3$ or $NaNO_2$.[11]

Results and Discussion

Photochemical Nitration of HBA. Excitation of nitrate ion at 313 nm in the presence of HBA in an aqueous alkaline solution gave a yellow solution with an absorption maximum at 406 nm. After extraction with ether, concentration, and TLC-separation, the photoproduct was identified as 4-hydroxy-3-nitrobenzoate, HNB, by ^{1}H NMR ($CDCl_3$) δ=8.74 (2H), 8.10 (5H), 7.30 (6H); IR

Table 1. Quantum Yield for Reactants Consumption (Φ_{-A}) and Absorbance Increase due to the Nitro-Compounds Formed (ΔA) by Photonitration ([$NaNO_3$]=0.2 M, pH=11, [A]=50 μM)

Compound, A	$\Phi_{-A}\times10^5$	ΔA (λ/nm)
o-Hydroxybenzoic acid	0.88	0.08(350)
m-Hydroxybenzoic acid	0.94	0.12(350)
p-Hydroxybenzoic acid	5.7	0.12(406)
p-Anisic acid	0.64	0.008(360)
Methyl 4-hydroxybenzoate	1.2	0.004(360)
Phenol	22	0.007(390)
p-Methoxyphenol	19	0.007(340)
p-Chlorophenol	21	0.005(350)
o-Cresol	11	0.005(350)
m-Cresol	29	0
p-Cresol	17	0

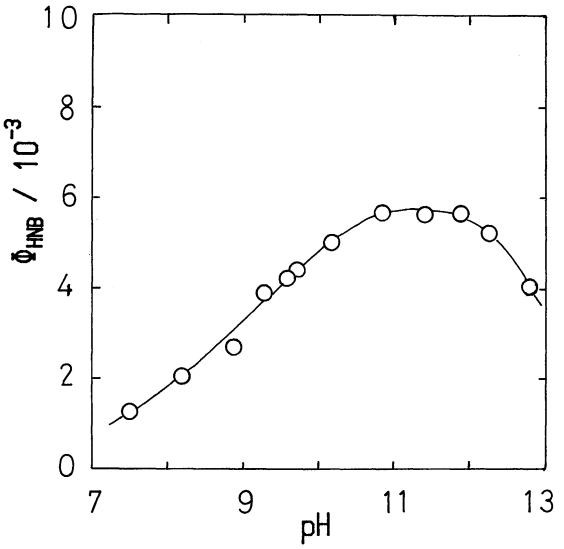

Fig. 1. Effect of pH on the Φ_{HNB} values. [HBA]=50 μM, [$NaNO_3$]=50 mM.

3400 cm^{-1} (–OH), 2500 and 2650 cm^{-1} ($-NO_2$), 1140 cm^{-1} (–COOH), 600, 670 and 1620 cm^{-1} (benzene ring); and UV(H_2O) 406 nm (ε: 4340 M^{-1} cm^{-1}, 1 M=1 mol dm^{-3}) via comparison with authentic HNB. Since the value of Φ_{-HBA} was almost equal to that of Φ_{HNB}, HNB was taken to be a main product. The Φ_{HNB} values depended on the temperature; 0.006 at 25 °C, 0.008 at 45 °C, and 0.011 at 55 °C.

The photonitration was examined also with other substitued benzoic acids and phenols, and the results are listed in Table 1. Here Φ_{-A} denotes the disappearance yield of a substrate (A) and ΔA is the absorbance of nitrated substrate, at the maximum wavelength shown in parenthesis, formed by 10 min irradiation.

Effect of pH on Φ_{HNB}. Figure 1 shows the pH effect on Φ_{HNB}, exhibiting a peak at pH around 11. The primary processes for the photodissociation of nitrate ion are expressed as follows:

$$NO_3^- + h\nu \longrightarrow NO_2 + O^{-}\cdot \quad (1)$$

$$O^{-}\cdot + H^+ \rightleftharpoons OH\cdot \quad (pK_a \text{ of } OH\cdot = 11.8) \quad (1')$$

$$NO_3^- + h\nu \longrightarrow NO_2^- + O \quad (2)$$

Process (1) is dominant at pH=11—13 and process (2) occurs at pH=8—10. The NO_2+$O^{-}\cdot$ formation is about ten times more efficient than the NO_2^-+O formation.[1-4] According to the mechanistic investigations using pulse radiolysis on a mixture of nitrate ion and phenol, NO_2 attacks the OH adduct of phenol followed by nitration.[12] The same mechanism seems to take place at pH around 10—12 in the present case. At pH<10 process (2) becomes predominant, and the Φ_{HNB} values decrease. On the other hand, at pH higher than 13, the equilibrium concentration of OH· becomes smaller due to process (1′) resulting in the lowering of the Φ_{HNB} values.

Effect of OH· Scavengers on Φ_{HNB}. KI, NaSCN, and NaBr react with OH· to form dihalogeno radical anions ($I_2^{-}\cdot$, $(SCN)_2^{-}\cdot$, and $Br_2^{-}\cdot$) and OH^- ion. The rate constants are 1.4×10^{10} for OH·+I^-, 6.6×10^9 for OH·+SCN^-, and 1.1×10^9 M^{-1} s^{-1} for OH·+Br^-.[13] Addition of 10 mM of the scavengers to the solution depressed the Φ_{HNB} value by 57% for KI, by 32% for NaSCN, and by 1% for NaBr. Although the degree of the depression is qualitatively in line with the order of rate constants mentioned above, this suggests that OH· reacts with HBA and the nitration reaction starts via processes (1) and (1′).[14]

Effect of HBA Concentration on Φ_{HNB} and Φ_{-HBA}. The results are shown in Fig. 2. At HBA concentrations below 50 μM, the Φ_{HNB} values are equal to the Φ_{-HBA} values, indicating a quantitative convertion of HBA into HNB. At higher HBA concentrations, the Φ_{-HBA} values are larger than Φ_{-HNB}. This may reflected the HBA decomposition because the irradiation light was absorbed by HBA. Assuming that the OH· radical reacts with HBA in competition with the processes as shown in Eq. 3 (i.e., the reverse processes of Eqs. 1 and 1′) and in Eq. 4, and that the HBA–OH adduct reacts with NO_2 to produce HNB, processes (3) through (6) take place in the photonitration:

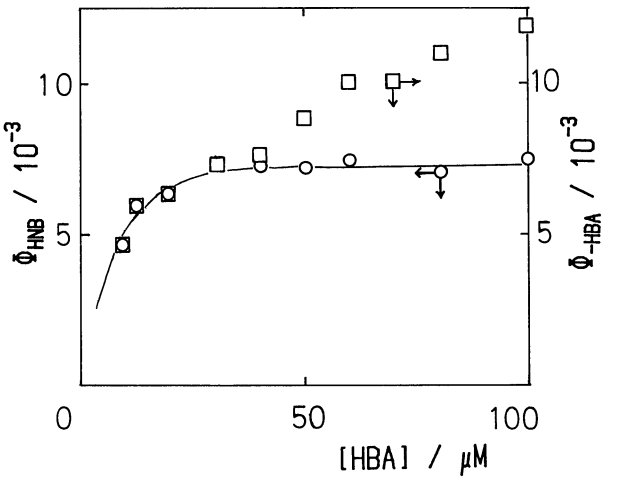

Fig. 2. Effect of HBA concentration on the Φ_{HNB} and Φ_{-HBA} values. [$NaNO_3$]=50 mM, pH=12.

$$OH\cdot + NO_2 \longrightarrow NO_3^- + H^+ \quad (3)$$

$$OH\cdot + NO_3^- \longrightarrow NO_3 + OH^- \quad (k_4 = 9.0\times10^7\ M^{-1}\ s^{-1}) \quad (4)$$

$$OH\cdot + HBA \longrightarrow HO\text{–}HBA \quad (k = 9.0\times10^9\ M^{-1}\ s^{-1}) \quad (5)$$

$$HO\text{–}HBA + NO_2 \longrightarrow HNB + H_2O \quad (6)$$

From these equations, the Φ_{-HNB} value is expressed by

$$\Phi_{HNB} = f_{OH}\frac{k[HBA]}{\beta_{OH} + k[HBA]}\alpha \quad (7)$$

where f_{OH} is the yield of OH· (or NO_2) radical production from nitrate ion via process (1), β_{OH} the pseudo first-order rate constant for the OH-disappearance reactions, and α the reaction probability of HBA–OH with NO_2, to form HNB.

A plot of $1/\Phi_{HNB}$ against 1/[HBA] gave a straight line and a value of 5×10^4 s^{-1} was obtained as β_{OH} from the ratio of the intercept to the slope, by use of the k value ($=9\times10^9$ M^{-1} s^{-1}).[12] The f_{OH} value was reported as 1.3—1.7×10^{-2} by Zepp and Zellner.[15,16] The α value was obtained to be 0.5 from the maximum quantum yield ($\Phi_{HNB}^{max}=f_{OH}\alpha=0.007$, [$NaNO_3$]=50 mM) at higher concentrations of HBA.

Even if OH· reacts with nitrate ion to form NO_3 and OH^- in concentrated solutions, OH· can be reproduced subsequently by the following reaction:[16]

$$NO_3 + H_2O = HNO_3 + OH\cdot \quad (k = 1.4\times10^2\ M^{-1}\ s^{-1}) \quad (8)$$

Although the stationary concentration of OH· should smaller in this case, OH· reacts with HBA and then the HO–HBA adduct reacts with NO_2.

Nitration of HBA by Excitation of Nitrite Ions. Photonitration of HBA was also observed by irradiating nitrite ion at 366 nm. In this case, the quantum yield was about ten times higher than that for NO_3^- excitation. The quantum yield decreased when OH· scavengers such

as methanol, ethanol, and 2-propanol were added. The effects of pH and the HBA concentration were similar to those in nitrate ions excitation. However, the reaction did not proceed in deaerated solutions, but was enhanced after addition of gasous NO_2.

From these observations, together with similar results obtained for nitration of butyl 4-hydroxy-3-benzoate, we could conclude that NO is oxidized to NO_2 by dissolved oxygen i.e.,[9,18]

$$NO_2^- + h\nu \longrightarrow NO + O^- \quad (9)$$

$$2NO + O_2 \longrightarrow 2NO_2 \quad (10)$$

Then, $OH\cdot$ and NO_2 radicals react with HBA, and subsequent processes (1′), (5), and (6) to give HNB. Referring to the mechanism of the reaction between the OH adduct of toluene and NO_2, an intermediate such as HO^-–HBA–NO_2^+ can be envisaged based on the electron abstraction by the HO–HBA adduct from the NO_2 group.[14] Therefore, the nitration at the meta position (3) in HBA's benzene ring is facilitated because of a higher electron density, and the dehydration results in process (6); these may apply to the irradiation experiments with nitrate and nitrite ions.

These results show that NO_2 is photochemically produced in the presence of a substrate reactive to $OH\cdot$. OH radicals are also produced on the surface of the ocean near the equator by the sunlight excitation of the nitrate or nitrite ion dissolved in the seawater. These radicals react further with bromide ion, for example, to give NO_x in the atmosphere above the ocean surface.[19–22]

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