Radiation-induced Degradation of Nitrobenzene in Aqueous Solutions

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Both the efficiency and pathways of nitrobenzene degradation induced by γ-ray irradiation were significantly influenced by the addition of reactive species scavengers. Experimental results showed that the degradation of nitrobenzene was more favorable under oxidative conditions than under reductive conditions. Based on the product analysis by GC–MS, possible degradation mechanisms of nitrobenzene under both oxidative and reductive conditions were proposed.

Nitrobenzene (NB), widely present in waste water from chemical industries, is a highly toxic compound.[1] Because of the strong electron-withdrawing character of the nitro-group, the biodegradability of NB is poor.[2] Therefore, conventional biotechnology is not effective for the treatment of NB-rich waste water. Utilization of ionizing radiation to treat waste water has a major advantage over other treatment methods: A complete degradation of NB can be achieved without consumption of any chemicals and resulting in no further pollution.[3–5] Radiolysis of NB aqueous solutions has been investigated, focusing on the determination of rate constants between NB and the reactive species generated from water radiolysis,[6] and the identification of the degradation products.[7–9] However, information about radiolytic decomposition of NB, especially reductive degradation with e_{aq}^- and H· and the identification of degradation products, is still sparse.[6–8,10] In this work, in order to clarify which species generated from water radiolysis play the key roles in the degradation of NB and to elucidate the mechanisms of NB degradation under both oxidative and reductive conditions, experiments were conducted to investigate the respective effects of addition of H_2O_2, *t*-BuOH and *i*-PrOH on the radiation-induced degradation of NB. Based on the analysis of the products, the degradation mechanisms of NB under both oxidative and reductive conditions were suggested.

All the reagents, purchased from Shanghai Chemical Reagent Co., were of analytical reagent grade and used without further purification, except that ethyl acetate was redistilled before use. Throughout the irradiation experiments, the samples were prepared with doubly distilled water in Pyrex glass vessels and irradiated by a ^{60}Co-γ-source with an activity of approximately 60 kCi (2.22×10^{15} Bq). The dose rate was determined by a Fricke-dosimeter using $G\,(\mathrm{Fe}^{3+}) = 15.6$.

NB concentration was determined by High Performance Liquid Chromatography (HPLC) (Agilent 1100, VWD detector) with an ODS column. The mobile phase was a mixture of water with 0.1% acetic acid and methanol (40:60) delivered at a flow rate of $1\,\mathrm{mL\,min^{-1}}$. The detecting wavelength was 254 nm. Total organic carbon (TOC) measurements were carried out using a TOC analyzer (TOC-V_{CPN}, Shimadzu Co.). Analysis of final products was performed on a GC–MS (an Agilent 6890 GC coupled with a Micromass MS) with a $30\,\mathrm{m} \times 0.25\,\mathrm{mm} \times 0.25\,\mu\mathrm{m}$ DB-5 column [Split ratio: 10:1; Injection temperature: 250 °C; Carrier gas: Helium ($1\,\mathrm{mL\,min^{-1}}$)]. The irradiated samples were extracted with ethyl acetate, and dehydrated with anhydrous magnesium sulfate for 24 h. Thereafter, the filtrate was concentrated using a spin evaporator. The extracts with a volume of 0.2-µL were subjected to GC-MS analysis.

Irradiation of dilute NB aqueous solutions produces several reactive species, such as ·OH, e_{aq}^- and H·. When reactive species scavengers, e.g., H_2O_2, *i*-PrOH or *t*-BuOH, were present, according to the principles of competitive kinetics, ·OH, e_{aq}^- or H· was discriminately scavenged. Figure 1 illustrates the influences of the addition of H_2O_2, *t*-BuOH or *i*-PrOH on the degradation efficiency of NB. There was an optimal H_2O_2 concentration at a certain dose rate for the degradation of NB, e.g., 20 mM H_2O_2 at a dose rate of $55.75\,\mathrm{Gy\,min^{-1}}$. This can be interpreted by the competition between NB and H_2O_2 for reactive species produced from water radiolysis. With the addition of appropriate amount of H_2O_2, the degradation efficiency of NB enhanced due to the conversion of e_{aq}^- to ·OH induced by H_2O_2. On the contrary, at an excessive dosage, H_2O_2 would compete with NB for ·OH. As a result, the degradation of NB was inhibited. As shown in Figure 1, with the addition of *i*-PrOH or *t*-BuOH, the NB degradation rate gradually reduced until it diminished to an invariable value. This is due to the removal of ·OH by *i*-PrOH or *t*-BuOH. Furthermore, the effect of *i*-PrOH on the degradation of NB was more drastic than that of *t*-BuOH, because *i*-PrOH removed not only ·OH but also H·. On the other hand, even if the removal of ·OH and H· was complete (with the addition of *i*-PrOH up to 30 mM), the NB solution still had a reduction rate of about 20%. Therefore, it can be concluded that e_{aq}^- played an important role in the reductive degradation of

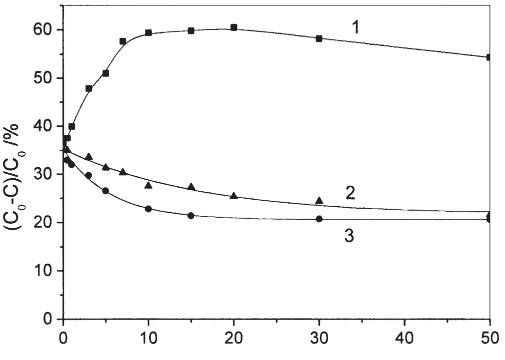
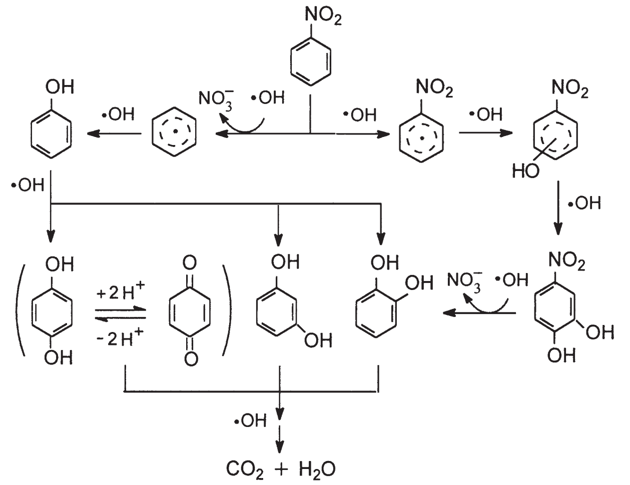


Figure 1. Effect of reactive species scavengers on the degradation of NB as a function of their concentration (Initial NB concentration (C_0): 2 mM, dose rate: $55.75\,\mathrm{Gy\,min^{-1}}$, irradiation time: 100 min, scavengers: 1: H_2O_2, 2: *t*-BuOH, 3: *i*-PrOH).

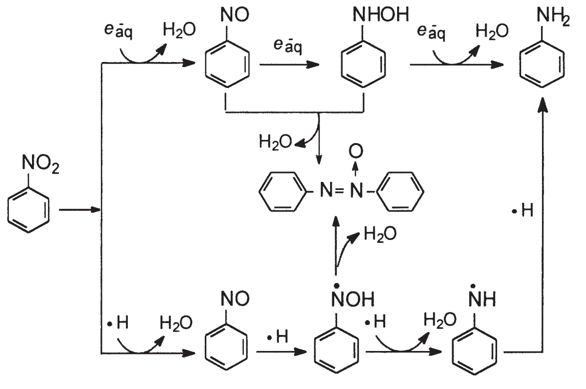
NB.

Under oxidative conditions, a gradual TOC reduction of NB solutions was found with increasing radiation dose. For instance, in the presence of 10 mM H_2O_2, the TOC concentration of NB solution reduced from initial 148.3 mg L^{-1} to final 79.8 mg L^{-1} after 160-min irradiation at a dose rate of 159.7 Gy min^{-1}. This result demonstrated the mineralization of NB to carbon dioxide and water. No obvious TOC reduction was observed when NB solutions were irradiated under reductive conditions.

Degradation pathways under oxidative conditions:



Degradation pathways under reductive conditions:



Scheme 1. Possible degradation pathways of NB induced by γ-ray irradiation.

The samples subjected to GC-MS determination were the extractions from NB solutions with addition of 10 mM H_2O_2 or 30 mM *t*-BuOH after 5 h irradiation at a dose rate of 55.75 Gy min^{-1}. The GC–MS analytic results indicated that the degradation products of NB were significantly different under the oxidative and reductive conditions. With the addition of H_2O_2, the main degradation products of NB were phenol (m/z 94.04), catechol (m/z 110.04), resorcinol (m/z 110.08), hydroquinone (m/z 110.04), *o*-nitrophenol (m/z 139.03), *m*-nitrophenol (m/z 139.03), *p*-nitrophenol (m/z 139.03), 4-nitrocatechol (m/z 155.02), and *p*-benzoquinone (m/z 108.02). With the addition of *t*-BuOH, the primary products were nitrosobenzene (m/z 107.04), aniline (m/z 93.06), and azoxybenzene (m/z 198.08). Based on the analysis of products, possible pathways of the NB degradation were presented in Scheme 1. In the presence of H_2O_2, the role of ·OH was predominant in the NB degradation. Initiated by ·OH, electron transfer and denitration occurred, leading to the formation of phenyl radicals and nitrophenyl radicals. The addition of ·OH to these radicals resulted in the formation of oxidative intermediate products. Ultimately, carbon dioxide and water were formed. In the presence of *t*-BuOH, the species crucial in the degradation of NB were e_{aq}^- and H·. Through hydrogenation and elimination, nitrosobenzene and aniline were formed. The combination of reactive intermediates during the deoxidization processes formed azoxybenzene. Complete mineralization cannot be achieved under reductive conditions.

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References

1 E. L. Kochany, *Chemosphere*, **22**, 529 (1991).
2 P. H. Nielsen and T. H. Christensen, *J. Contam. Hydrol.*, **17**, 55 (1994).
3 A. Sakumoto and T. Miyata, *Radiat. Phys. Chem.*, **24**, 99 (1984).
4 N. Getoff, *Radiat. Phys. Chem.*, **54**, 377 (1999).
5 A. K. Pikaev and V. N. Shubin, *Radiat. Phys. Chem.*, **24**, 77 (1984).
6 K.-D. Asmus, A. Wigger, and A. Henglein, *Ber. Bunsen-Ges. Phys. Chem.*, **70**, 862 (1966).
7 H. Loebl, G. Stein, and J. Weiss, *J. Chem. Soc.*, **1950**, 2704.
8 R. W. Matthews and D. F. Sangster, *J. Phys. Chem.*, **71**, 4056 (1967).
9 J. A. Knight, *Radiat. Res.*, **52**, 17 (1972).
10 C. N. Kurucz, T. D. Waite, S. E. Otano, W. J. Cooper, and M. G. Nickelsen, *Radiat. Phys. Chem.*, **65**, 367 (2002).

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