

Photodegradation of nitrobenzene using 172 nm excimer UV lamp

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Abstract

Photodegradation of nitrobenzene (NB) using an excimer UV lamp at a wavelength of 172 nm is investigated. Experimental results show that high concentration nitrobenzene can be efficiently degraded with irradiation by excimer UV lamp, and confirm that degradation of nitrobenzene is more efficient by UV/H₂O₂ combination than UV only. In the case of using UV only, 60 min of treatment was found to be sufficient to degrade the major part of NB solution with a concentration of less than 4 mM. In the case of using the combination of UV/H₂O₂ with a H₂O₂ concentration of 7:1 molar ratio to NB, 4.07 mM NB solution drastically decreased to 0.41 mM after treatment for only 20 min. Degradation intermediate products are identified by analyzing the degradation products with GC/HRMS and possible degradation pathways of nitrobenzene are suggested.

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Keywords: Degradation; Nitrobenzene; Excimer UV lamp; GC/HRMS

1. Introduction

Nitrobenzene (NB) is considered to be a highly toxic aromatic compound which is widely used in explosives, pesticides, prepharmo, dye production and so on. The strong electron-deficient character of its nitro-group results in nitrobenzenes resistant to oxidation by biological treatment and conventional chemical oxidation [1–8]. Therefore, various alternative treatment technologies have been developed over the last two decades in order to cost-effectively meet environmental regulatory requirements. One such group of technologies is commonly referred to as advanced oxidation process, including UV light, solar light, γ -ray, etc. [9–21].

In general, conventional UV sources such as low or high pressure mercury lamps have low removal rates for many environmental contaminants. In 1993, a new generation of lamps was developed, based on the excited dimmer (excimer) mechanism [22]. These lamps are capable of producing high power, high efficiency and narrow band radiation from the near UV ($\lambda = 354$ nm) to deep UV ($\lambda = 126$ nm). On the other hand, they have some characteristic features such as incoherence, almost-monochromaticity, more than 22 wavelengths, high UV and VUV intensities, large area processing enabled ($\text{cm}^2\text{-m}^2$), oper-

ation at low temperature, robust and inexpensive system, ecologically beneficial, free of mercury, no electrodes in discharge gap, long life, etc. [23–24].

Kogelschatz and Niwano et al. [25–27] first utilized excimer UV source applications in wastewater treatment and they have proposed designs for photoreactors incorporating excimer UV lamps as integrated elements, probably at specific VUV/UV wavelengths, to be practical or commercial interest. These excimer UV lamps have enormous potential for industrial applications because of its simplicity, high efficiency and low cost. In the course of a comparative investigation on advanced oxidation processes for the treatment of NB, in this paper we report the degradation of NB by using a 172 nm radiation from a Xe₂* (7.21 eV) excimer UV lamp. This work will form a basis for the application to the industrial wastewater containing nitrobenzene.

2. Experimental

2.1. Materials and photodegradation experiments

NB, ethyl acetate and hydrogen peroxide (35%), all purchased from Shanghai Chemical Reagent Company, were of analytical reagent grade. NB was redistilled at 210.8 °C under atmospheric pressure before use and ethyl acetate was used after purifying by appropriate methods. Double distilled water was used throughout the experiments. Quartz glass vessels and excimer UV lamp [23] at 172 nm were made in house.

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Throughout the experiments, the samples were prepared with double distilled water in Pyrex glass vessels and fully dissolved by ultrasonic before use. Then 60 mL of NB solution was displaced and put into a quartz glass vessel for each sample and irradiated by 172 nm excimer UV lamp for different periods of time. In view of the fact that the path along which 172 nm light penetrates the water is very short due to its high absorption coefficients ($<1.8 \text{ cm}^{-1}$ at 25°C) and the intensity of the 172 nm VUV light will decrease nearly 90% in 5 mm thickness of water [28], a dynamic photodegradation system was designed in which NB aqueous solution was always circulating through a pump.

2.2. Analytical methods

The UV–vis absorption spectra of NB solutions and NB concentration were recorded by a UV–vis spectrophotometer (UV-2401PC, Shimadzu Co.). A GC system (Agilent 6890) with $30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \mu\text{m}$ DB-5 column coupled to a TOF-MS (GCT, Micromass Co., Manchester, UK) was used to identify the degradation products. The mass spectra were recorded on the GCT in EI mode at a resolution of 7000 FWHM and nominal electron energy of 70 eV. Temperatures of the MS source, interface and GC injector were set at 200, 250 and 280°C , respectively. Helium was used as the carrier gas at a velocity of 1.0 mL/min. The column temperature was programmed as follows: isothermal 150°C for 0.5 min, then heated up to 280°C at a rate of $20^\circ\text{C}/\text{min}$, held for 3 min. GCT was equipped with the NIST98 standard EI spectra library containing approximately 130,000 mass spectra. Sample analysis, accurate mass measurement and elemental composition determination were performed automatically using the OpenLynx software within MassLynx.

Before being subjected to GC–MS analysis, the samples, taken from the 2.44 mM NB solution irradiated by 172 nm excimer UV lamp for 30 or 40 min, were extracted by ethyl acetate, and then dehydrated by anhydrate sodium sulfate for 5 min. The filtrate was then concentrated to 1 ml using a rotary evaporator. TOC was determined with a Shimadzu TOC-5000 total organic carbon analyzer.

3. Results and discussion

3.1. Direct photodegradation of NB by UV in aqueous solution

Fig. 1 illustrates the typical UV–vis spectra of the treated NB solution at an initial NB concentration of 2.44 mM; the samples were irradiated for 0, 5, 15, 20, 30, 40, 60 and 70 min. As shown in Fig. 1, the absorbance band at 268 nm decreased as exposure time increased. Further support for this result is shown in Figs. 2 and 3, which illustrate the degradation of NB with irradiation time at different initial NB concentrations. As shown in Figs. 1 and 2, although 60 min of treatment was found to be sufficient to degrade the major part of nitrobenzene, it would be necessary to continue the treatment for longer periods of time, to obtain a total degradation of nitrobenzene, especially when the initial concentration of NB was much more than 4 mM.

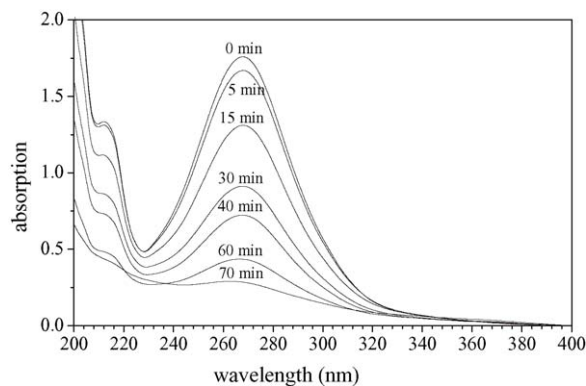


Fig. 1. UV absorption spectra of the treated NB with irradiation at different time periods by 172 nm excimer UV lamp (Initial NB concentration: 2.44 mM).

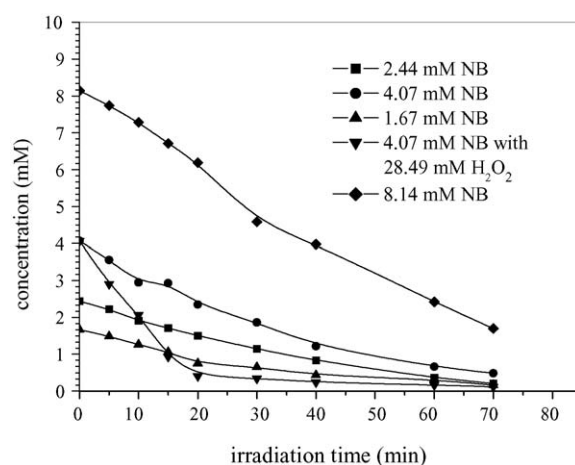


Fig. 2. The degradation of NB with irradiation time at different initial concentrations of NB by 172 nm excimer UV lamp.

3.2. Photodegradation of NB by the UV/H₂O₂ combination process

In order to achieve desired degradation efficiency in a reasonable time profile, hydrogen peroxide was employed to promote the photodegradation of NB in aqueous solution. Fig. 4 presents

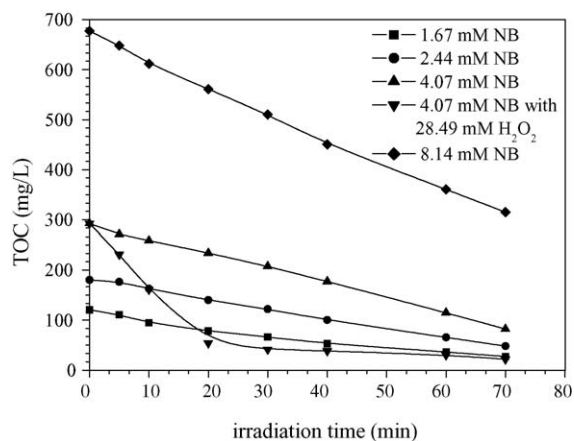


Fig. 3. Variation of TOC concentration of NB solution with irradiation time at different initial concentration of NB by 172 nm excimer UV lamp.

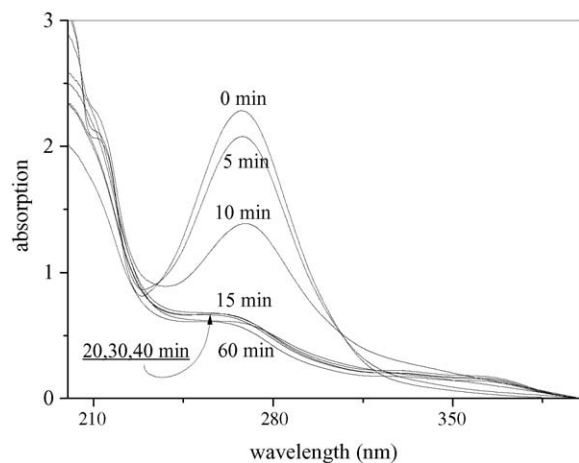


Fig. 4. UV absorption spectra of the treated NB with irradiation at different time periods by 172 nm excimer UV lamp in the presence of H_2O_2 (initial NB concentration: 4.07 mM; H_2O_2 concentration: 7:1 molar ratio to NB).

the absorption spectra of the treated NB solution at an initial NB concentration of 4.07 mM with irradiation at different time periods by 172 nm excimer lamp in the presence of H_2O_2 (H_2O_2 concentration: 7:1 molar ratio to NB). Compared with the application of UV only (Fig. 1), the combination of hydrogen peroxide with UV radiation (UV/ H_2O_2) is more effective in the degradation of the pollutant. More detailed results can be clearly found from one of the curves (with marks of ▼) in both Figs. 2 and 3 that 4.07 mM NB solution drastically decreased to 0.41 mM after treatment for only 20 min by combination of UV/ H_2O_2 with a H_2O_2 concentration of 7:1 molar ratio to NB. The experiment results showed that the degradation rate increased with the H_2O_2 concentration in the range of 1–7 molar ratios of hydrogen peroxide/nitrobenzene. As illustrated in Fig. 3, TOC removal of the solution is drastically accelerated by H_2O_2 . The increase of degradation rate of photodegradation of NB with the increase of H_2O_2 concentration is probably due to more hydroxyl radicals formed because H_2O_2 absorbs most of the incident light at a higher concentration. NB is attacked either by UV photon flow or hydroxyl radicals generated in H_2O_2 -photolysis. As the H_2O_2 concentration is increased, more hydroxyl radicals are available to attack the aromatic ring. Mean-

while, hydroxyl radicals can reversely recombine into hydrogen peroxide. Moreover, it should be noted that the excess of spiked H_2O_2 likely acts as OH^\bullet scavenger to produce the much less reactive hydroperoxyl radicals (HO_2^\bullet), which consequently causes the decrease of the degradation rate of NB [29]. Accordingly in our work the experiment results show an optimal value for the hydrogen peroxide/nitrobenzene ratio of 7:1 molar ratio.

3.3. Identifications of degradation products by high resolution mass spectrometry

In order to clarify the pathways of NB degradation, the degradation products were identified by GC–EI–HRMS (high resolution mass spectrometry). Accurate mass measurements for all the molecular ions and fragment ions of the degradation products were obtained by external calibration and single point lock–mass correction at m/z 218.9856 using heptacosafuorotributylamine (PFTBA) as internal reference. The structures of all the degradation products were identified not only by the spectra library search (Match factors in Table 1) but also by the MS fragment assignments as well as the molecular ion determinations (see below). It should be noted that most of the match factors (Table 1) from the library search are not up to over 900, because the standard spectra in the NIST98 library were taken from quadrupole-MS rather than TOF-MS. However, the library search results can be used as one of the several evidences for structural identifications, especially for distinguishing between isomers, such as nitrophenols.

3.3.1. Molecular ions of the degradation products

Relative concentrations from total ion chromatograph (TIC), accurate masses of molecular ions and assigned molecular formulae for the degradation products of NB measured by GC–EI–HRMS are summarized in Table 1. As indicated in the table, the main degradation products in the degradation of nitrobenzene are hydroxylated products and their derivatives, including nitrophenol, nitrocatechol, benzenediol, phenol and benzoquinone, of which the presences of the three nitrophenol isomers have been also reported by other authors [30–32]. Furthermore, possible further products of cleavage are not detected under photocat-

Table 1
Relative concentrations, accurate masses of molecular ions and assigned molecular formulae for the degradation products of NB measured by GC–EI–HRMS (initial nitrobenzene concentration: 4.07 mM)

t_R (min)	RC ^a (%)	Measured mass (Da)	RA ^d (%)	Calculated mass (Da)	Error (mDa, ppm)	Molecular formulae	Predicted products	Match factor
2.29	0.51 ^b	108.0217	100	108.0211	0.6, 5.3	$\text{C}_6\text{H}_4\text{O}_2$	<i>p</i> -Benzoquinone 1	882
2.51	0.77 ^b	94.0416	100	94.0419	−0.3, −2.8	$\text{C}_6\text{H}_6\text{O}$	Phenol 2	947
3.49	0.64 ^b	139.0275	100	139.0269	0.6, 4.0	$\text{C}_6\text{H}_5\text{NO}_3$	<i>o</i> -Nitrophenol 3	771
3.90	1.12 ^c	110.0356	100	110.0368	−1.2, −10.7	$\text{C}_6\text{H}_6\text{O}_2$	1,2-Benzenediol 7	880
4.43	1.56 ^c	155.0205	100	155.0219	−1.4, −8.8	$\text{C}_6\text{H}_5\text{NO}_4$	<i>p</i> -Nitrocatechol 6	259
4.47	2.31 ^c	110.0339	100	110.0368	−2.9, −26.2	$\text{C}_6\text{H}_6\text{O}_2$	Hydroquinone 8	682
5.92	0.13 ^b	139.0280	100	139.0269	1.1, 7.6	$\text{C}_6\text{H}_5\text{NO}_3$	<i>m</i> -Nitrophenol 4	832
6.31	0.086 ^b	139.0281	100	139.0269	1.2, 8.3	$\text{C}_6\text{H}_5\text{NO}_3$	<i>p</i> -Nitrophenol 5	713

^a RC: relative concentration of degradation products.

^b Irradiation time 30 min.

^c Irradiation time 40 min.

^d RA: relative abundance expressed as percentage of base peak.

alytic conditions, and pointed to a rapid mineralization to CO₂ and H₂O from these compounds. Table 1 also indicates that the relative concentrations of the degradation products remain at very a low level when NB (initial 4.07 mM) was under irradiation for 30 or 40 min. It is interesting that the relative concentration (0.77%) of phenol is almost equal to the sum of those of *o*-nitrophenol (0.64%), *m*-nitrophenol (0.13%) and *p*-nitrophenol (0.086%) as NB was irradiated for 30 min. On the other hand, the relative concentrations of the degradation products have a little increase as the irradiation time was prolonged to 40 min, examples include 1,2-benzenediol (1.12%), *p*-nitrocatechol (1.56%) and hydroquinone (2.31%). The results will be further discussed in detail below. The mass accuracy for all the molecular masses is within ±3 mDa or below 11 ppm (except product **8**), which confirms the molecular ions and molecular formulae for all the degradation products. The molecular ions m⁺ for all the products are observed in their spectra as the base peaks (100%), which implies that all the products are quite stable due to the resonance stabilization.

3.3.2. Fragmentations of the degradation products

Accurate masses and their corresponding assigned elemental compositions of fragment ions from each spectrum of the products together with their relative abundances, are summarized in Table 2. The mass accuracy for these fragment masses, determined relative to the values calculated from their assigned elemental compositions, was always better than ±3 mDa.

All the fragmentation pathways proposed for formations of the MS fragments of all the degradation products are established in order to confirm the structures of the products. Three of them, *p*-benzoquinone (**1**), *p*-nitrophenol (**5**) and 1,2-benzenediol (**7**), are taken as examples as shown in Fig. 5 and assigned as follows.

Product **1** (*p*-benzoquinone): The initial pathway involves an α-cleavage of the C=O group from the molecular ion (**1m**) to form an open chain radical cation, which then expels double CO (28 Da) to form fragments **1b** (33.4%) and **1d** (13.2%) or eliminates C₂H₂ (26 Da) to form fragment **1a** (38.6%), followed

Table 2
Accurate masses and assigned elemental compositions for fragment ions of the degradation products measured by GC–EI–HRMS (initial nitrobenzene concentration: 4.07 mM)

Fragments	Measured mass (Da)	RA (%)	Calculated mass (Da)	Error (mDa)	Elemental compositions
1a	82.0068	38.6	82.0055	1.3	C ₄ H ₂ O ₂
1b	80.0262	33.4	80.0262	0	C ₅ H ₄ O
1c	54.0218	50.9	54.0106	2.2	C ₃ H ₂ O
1d	52.0329	13.2	52.0313	1.6	C ₄ H ₄
2a	66.0485	19.4	66.0470	1.5	C ₅ H ₆
2b	65.0416	15.7	65.0391	2.5	C ₅ H ₅
2c	39.0261	5.5	39.0235	2.6	C ₃ H ₃
3a	122.0270	2.9	122.0242	2.8	C ₆ H ₄ NO ₂
3b	109.0343	17.0	109.0290	1.4	C ₆ H ₅ O ₂
3c	81.0351	14.4	81.0340	1.1	C ₅ H ₅ O
3d	65.0403	16.1	65.0391	1.2	C ₅ H ₅
3e	39.0256	10.1	39.0235	2.1	C ₃ H ₃
4a	93.0353	36.6	93.0340	1.3	C ₆ H ₅ O
4b	65.0403	47.2	65.0391	1.2	C ₆ H ₅
4c	39.0261	14.1	39.0235	2.6	C ₃ H ₃
5a	109.0292	38.2	109.0290	0.2	C ₆ H ₅ O ₂
5b	93.0342	13.9	93.0340	0.2	C ₆ H ₅ O
5c	81.0352	16.4	81.0340	1.6	C ₅ H ₅ O
5d	65.0399	43.3	65.0391	0.8	C ₅ H ₅
5e	53.0397	4.1	53.0391	0.6	C ₄ H ₅
5f	39.0261	14.8	39.0235	2.6	C ₃ H ₃
6a	107.0119	61.2	107.0133	−1.4	C ₆ H ₃ O ₂
6b	93.0227	11.1	93.0215	1.2	C ₅ H ₃ NO
6c	79.0205	13.4	79.0184	2.1	C ₅ H ₃ O
6d	51.0260	2.1	51.0235	2.5	C ₄ H ₃
7a	109.0301	1.1	109.0290	1.1	C ₆ H ₅ O ₂
7b	81.0370	6.7	81.0340	3.0	C ₅ H ₅ O
7c	64.0336	15.3	64.0313	2.3	C ₅ H ₄ O
7d	53.0421	2.2	53.0391	3.0	C ₄ H ₅
8a	82.0432	8.9	82.0419	1.3	C ₅ H ₆ O
8b	81.0346	13.7	81.0340	0.6	C ₅ H ₅ O
8c	53.0409	2.8	53.0391	1.8	C ₄ H ₅
8d	39.0256	1.2	39.0235	2.1	C ₃ H ₃

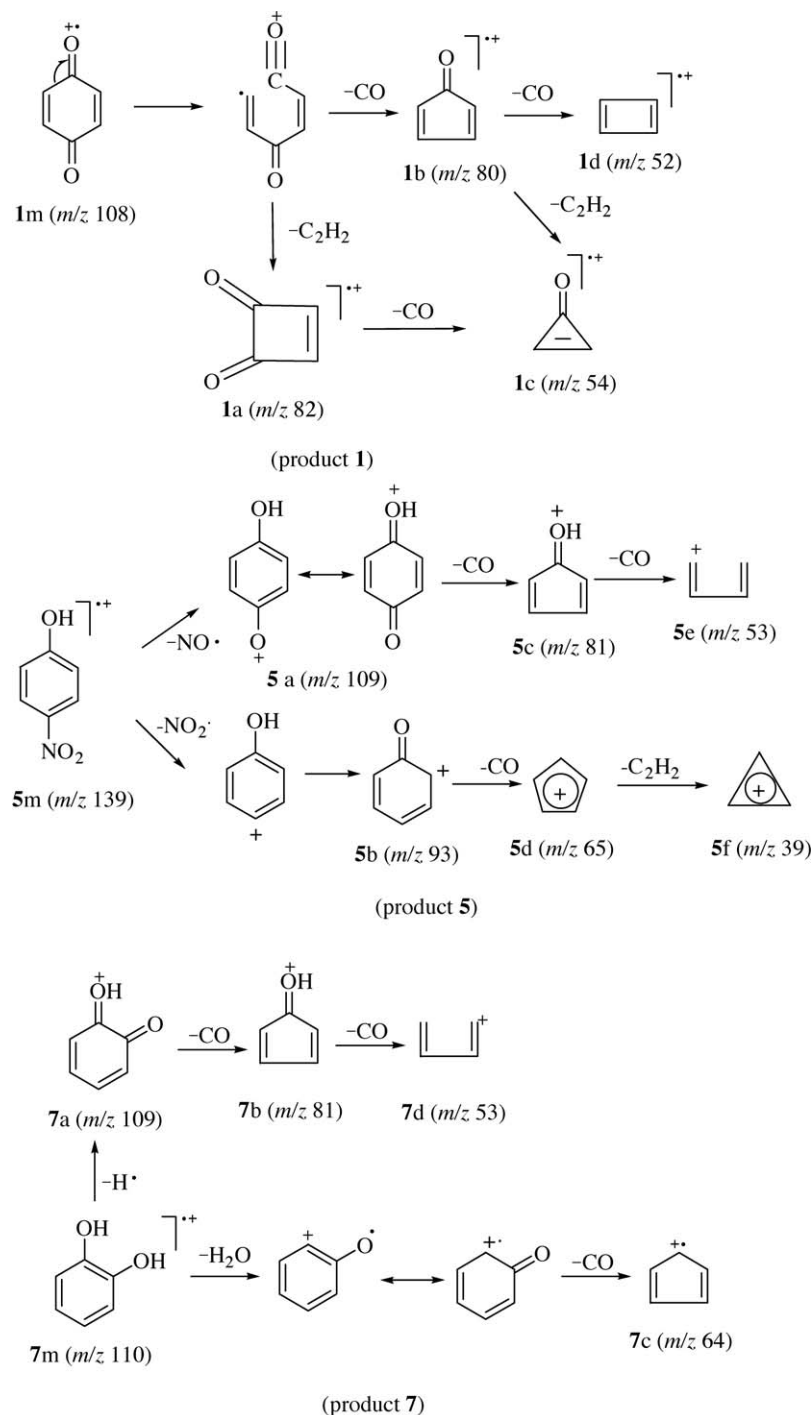


Fig. 5. Proposed fragmentation pathways for the exemplary degradation products **1**, **5** and **7** (cf. Table 2).

by the loss of CO to form fragment **1c** (50.9%). **1c** can also be formed from **1b** by the loss of C_2H_2 .

Product **5** (*p*-nitrophenol): Loss of NO radical from the molecular ion (**5m**) of product **5** afforded cation **5a** (38.2%) with a resonance structure, which then eliminates double CO to form fragments **5c** (16.4%) and **5e** (4.1%). Loss of NO_2 radical from the molecular ion (**5m**) afforded a phenol cation which then transformed into cation **5b** via a H-transfer. Cation **5b** was further fragmented by loss of

CO and C_2H_2 to yield cation **5d** (43.3%) and **5f** (14.8%), respectively.

Product **7** (1,2-benzenediol): Loss of H radical from the molecular ion (**7m**) of product **7** afforded cation **7a** with a weak abundance (1.1%), which then eliminated double CO to form cations **7b** (6.7%) and **7d** (2.2%). Loss of H_2O from the molecular ion (**7m**) yielded a radical cation with a resonance structure, which was further fragmented by loss of CO to give radical cation **7c** (15.3%).

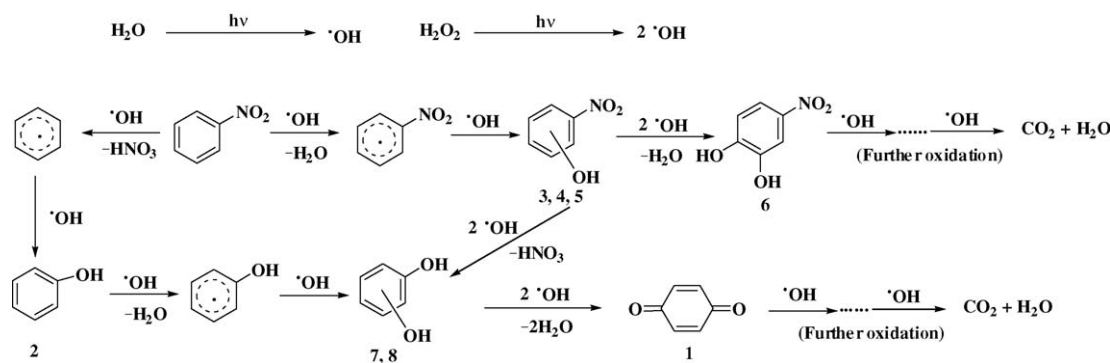


Fig. 6. Possible degradation pathways of NB induced by 172 nm excimer UV lamp irradiation (H_2O_2).

3.4. Photodegradation pathways

By GC–HRMS, the aromatic degradation products were primarily identified to be 2-nitrophenol, 3-nitrophenol, 4-nitrophenol, 4-nitrocatechol, phenol, 1,2-benzenediol, hydroquinone and *p*-benzoquinone. In fact, the degradation mechanism of organic substances is often very complex. Some reactive intermediates might undergo further reactions and be present at undetectable concentrations. Hence, their transient existence can only be inferred from the kinetic data and/or other means.

From Table 1 we can see that only a small amount of degradation products can be accumulated over the whole irradiation time. In terms of the relative concentrations of the identified aromatic degradation products 1–8 from the parent molecules, the concentration of NB relative to the degradation products always remains at a high level as observed from TIC mentioned above. In a word, the degradation products of NB are more easily photolytic than their parent molecule.

It was noted that the main organic degradation products identified in the process are hydroxylated products and their derivatives such as phenolic compounds. This finding strongly suggests that a predominant high redox potential of OH^\bullet ($E^0 = 2.8 \text{ V}$) radical can be generated by the irradiation of dilute nitrobenzene aqueous solutions using Excimer UV Lamp Xe_2^* (7.21 eV) at 172 nm. As a result, OH radical played the most crucial role in the degradation of NB and the degradation products. Actually, hydroxyl radicals are even generated in natural waters under the influence of sunlight [33].

OH^\bullet can readily attack the benzene ring of NB at the carbon carrying a nitro-group as well as α -, β -or/and γ -carbons via electrophilic addition. If the attacks occur at α , β and γ -carbons, 2-nitrophenol, 3-nitrophenol and 4-nitrophenol were formed while the protons were eliminated from the new adducts. Likewise, if OH^\bullet attacks the carbon carrying a nitro-group, phenol and/or its derivatives were generated while the nitrate ions were released by the radical addition-elimination. Further degradations can occur to produce other organic substances in case that OH^\bullet radicals react with phenol, nitrophenol or/and other intermediates. In other words, the hydroxyl radicals, which take different attacking approaches mentioned above, may be coupled with each other in some complex way.

In the case of the presence of H_2O_2 , more hydroxyl radicals are available. Initiated by OH^\bullet radical, electron transfer

and denitration occurred, leading to the formation of phenyl radicals and nitrophenyl radicals. Accordingly the addition of OH^\bullet to those intermediates resulted in the formations of 2-nitrophenol, 3-nitrophenol, 4-nitrophenol, 4-nitrocatechol, phenol, 1,2-benzenediol, hydroquinone and *p*-benzoquinone. Finally, CO_2 and H_2O formed after further oxidation. Based on the degradation products by GC–HRMS analysis, possible degradation pathways are proposed in Fig. 6.

4. Conclusion

- One hundred and seventy-two nanometer UV excimer lamp is very effective in the degradation of pollutant nitrobenzene and the combination of hydrogen peroxide with UV radiation was found to be more effective than the application of only UV radiation in the degradation of the pollutant. This method is potentially useful for the applications to the industrial wastewater containing nitrobenzene.
- In the case of using UV only, 60 min of treatment was found to be sufficient to degrade the major part of NB solution with a concentration of less than 4 mM. However, it would be necessary to continue the treatment for longer periods of time to obtain a total degradation of NB, especially when the initial concentration of NB is much more than 4 mM.
- In the case of using the combination of UV/ H_2O_2 with a concentration of 7:1 molar ratio to NB, 4.07 mM NB solution drastically decreased to 0.41 mM after treatment for only 20 min. TOC removal of the solution is drastically accelerated by H_2O_2 . The degradation rate increased with the H_2O_2 concentration in the range of 1–7 molar ratios of $\text{H}_2\text{O}_2/\text{NB}$. The optimal value of the ratio of $\text{H}_2\text{O}_2/\text{NB}$ is 7:1.

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