

# Decomposition of dinitrotoluene isomers and 2,4,6-trinitrotoluene in spent acid from toluene nitration process by ozonation and photo-ozonation

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## Abstract

Ozone and UV/O<sub>3</sub> were employed to mineralize dinitrotoluene (DNT) isomers and 2,4,6-trinitrotoluene (TNT) in spent acid from toluene nitration process. The oxidative degradation tests were carried out to elucidate the influence of various operating variables on the performance of mineralization of total organic compounds (TOC) in spent acid, including reaction temperature, intensity of UV (254 nm) irradiation, dosage of ozone and concentration of sulfuric acid. It is remarkable that the nearly complete mineralization of organic compounds can be achieved by ozonation combined with UV irradiation. Nevertheless, the hydroxyl radicals ( $\cdot\text{OH}$ ) would not be generated by either ozone decomposition or photolysis of ozone under the experimental condition of this study. According to the spectra identified by gas chromatograph/mass spectrometer (GC/MS) and further confirmed by gas chromatograph/flame ionization detector (GC/FID), the multiple oxidation pathways of DNT isomers are given, which include *o*-, *m*-, *p*-mononitrotoluene (MNT) and 1,3-dinitrobenzene, respectively. In addition, oxidative degradation of 2,4,6-TNT leads to a 1,3,5-trinitrobenzene intermediate.

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**Keywords:** Ozonation; UV/O<sub>3</sub>; Dinitrotoluene; 2,4,6-Trinitrotoluene; Spent acid

## 1. Introduction

Due to the importance of nitrotoluenes, which are intermediates for dyes and pharmaceuticals as well as being precursors for the explosive 2,4,6-TNT, the toluene nitration process using a mixture of sulfuric and nitric acid has been well developed. The purpose of sulfuric acid is not only to promote formation of nitronium ion ( $\text{NO}_2^+$ ) but also to enhance solubility between the aqueous and organic phases [1]. On account of accumulation of water byproduct and existence of little amounts of DNT isomers and 2,4,6-TNT, the spent mixed acid needs to be treated industrially by sequential steps, including purification and concentration procedures [2]. In our previous publications [3,4], it has been concluded that the ingredients of DNT isomers dissolving in spent acid are in equilibrium with those of the organic product.

In the past, the oxidative degradation of organic compounds in spent acid was conducted by hydrogen peroxide, ozone [5,6] and potassium permanganate [7,8]. Nonetheless, by heating procedures Parks and Martin [9] converted organic compounds into higher molecular weight nitroaromatic compounds which would be removed by distillation columns sequentially. According to the studies of Chou et al. [10,11], the organic compounds dissolving in spent acid were destructed into carbon dioxide by electrochemical oxidation at Pt electrode.

The explosive compounds (e.g. 2,4-DNT, 2,4,6-TNT) should be destructed on account of their toxicity and possible carcinogenicity [12,13]. Therefore, the oxidative degradation of nitroaromatic compounds in wastewater from toluene nitration process has gained much attention. In one respect, Fenton's reagent was usually used to mineralize 2,4-DNT [14,15] and 2,4,6-TNT [16,17]. Based on the study of Oh et al. [18], the Fenton oxidation efficiency of TNT was enhanced on addition of  $\text{Fe}^0$ , which reduced the nitro groups of TNT to amino groups. In another respect, photo-assisted chemical oxidation manners have been utilized to remove the nitroaromatic compounds in wastewater. Ho [19] studied the mineraliza-

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tion of 2,4-DNT into carbon dioxide by UV/H<sub>2</sub>O<sub>2</sub>. Several researchers have been issued on the mineralization of TNT by combination of UV and H<sub>2</sub>O<sub>2</sub> [20–22]. In some technical report, Li et al. [23] used UV/Fenton's reagent for remediation of nitroaromatic explosives, of which order of reaction rate was 2-nitrotoluene > 4-nitrotoluene > 2,4-DNT > 2,6-DNT > TNT. According to the study by Beltrán et al. [24], the reaction temperature and pH value have a positive effect on the ozonation rate of 2,6-DNT, of which reaction with ozone contributes slightly to the ozonation rate. Additionally, radiation with the UV light and addition of hydrogen peroxide enhanced the ozonation rate of 2,6-DNT [25]. Currently, Liou et al. [26] has investigated the oxidative degradation of 2,4-DNT and TNT, of which oxidation rates were promoted by UV irradiation.

Until now, numerous studies have deal with the oxidative degradation of nitroaromatic explosives in wastewater, whereas the mineralization of those compounds in spent acid has been rarely discussed. In our previous work [27], it has been indicated that the nitroaromatic compounds in spent acid, e.g. 2,4-DNT, 2,6-DNT, 2,3-DNT, 3,4-DNT and 2,4,6-TNT, could be completely destructed by Fenton oxidation, of which oxidation efficiency is superior to that of UV/H<sub>2</sub>O<sub>2</sub>. In this research, the mineralization of DNT isomers and 2,4,6-TNT in spent acid was performed by ozonation and photo-ozonation to avoid diluting the concentration of spent acid. The effects of reaction temperature, intensity of UV irradiation, dosage of ozone and concentration of sulfuric acid on the mineralization efficiency of total organic compounds were also elucidated. Besides, the oxidation pathways of DNT isomers and 2,4,6-TNT would be explored simultaneously.

## 2. Experimental methods

### 2.1. Ozonation testing

The experiments were conducted in a batch-wise system (see Fig. 1) under atmospheric pressure at 288, 303 and 313 K, respectively. Prior to tests, a proportionate amount of spent acid (pH –1.4, rendered by military ammunition plant) was situated in the reactor (PIIN JIA Technology Co. JC-A18 Model). The appropriate amount of ozone in the oxygen stream was supplied by an ozone generator (Cosmos Tong Guang Scientech Co., Ltd. OG-4PW Model). The quartz reactor was equipped with cooling coils, connected to a circulating water bath (VWR Scientific Co. 1167 Model), to control the reaction temperature. One multi-point thermocouple (Multiprobe Switchbox Model HH-20-SW, Microprocessor Thermometer Model HH22 OMEGA, ±0.1 K) was inserted into the reaction zone for reading and controlling the temperature. Ozone was bubbled into the spent acid and mixed well with each other by using a propeller (850 ± 50 rpm). The compositions of spent acid were 74.3% H<sub>2</sub>SO<sub>4</sub>, 2.7% HNO<sub>3</sub>, 22.49% H<sub>2</sub>O and 0.51% TOC on the weight basis. During the course of ozonation, the spent acid was periodically sampled from the reactor and undergone TOC analysis to evaluate the residual organic compounds content.

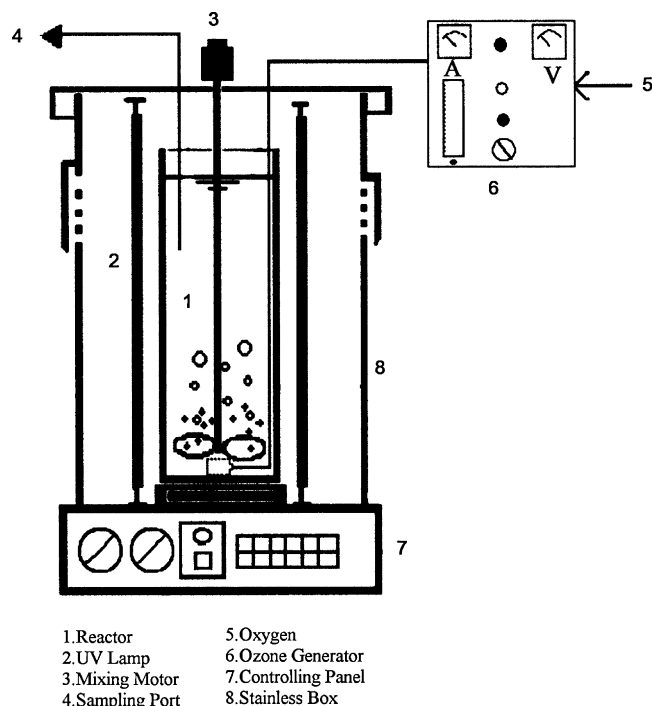


Fig. 1. Schematic diagram of the experimental apparatus employed in this work.

### 2.2. Photo-ozonation testing

Experiments were performed in the same apparatus as described in previous paragraph, wherein twelve low-pressure mercury vapor lamps (8 W each) were used as the light source at the wavelength of 254 nm (SANKYO Germicidal Lamps). The operating procedures of photo-ozonation tests were identical to those of ozonation as mentioned, whereas the UV lamps surrounding the centered reactor were all kept on during the testing. To elucidate the effect of UV irradiation on the destruction of organic compounds, four tests with various light intensities (0 up to 96 W) were carried out. In addition, for the sake of exploring the influence of dosage of ozone on the removal of organic compounds, a series of tests with various dosage of ozone (0 up to 3.8 g h<sup>-1</sup>) were undertaken. Besides, photo-ozonation tests were also conducted under atmospheric pressure at 312 K in the sulfuric acid concentration of 50, 66 and 74 wt.%, respectively to find out the optimal conditions upon mineralization of organic compounds.

To further investigate the effect of ferrous ions (UV/O<sub>3</sub>/Fe<sup>2+</sup>) on the mineralization of organic compounds, three tests with various concentration of ferrous ions (0 up to 0.1 M) were performed, wherein proportionate amounts of iron(II) sulfate heptahydrate (≥99.5%, Fluka) were added into the spent acid.

### 2.3. Total organic compounds analysis (TOC)

The spent acid undergone ozonation or photo-ozonation tests was analyzed using a Tekmar Dohrmann Phoenix 8000 instrument equipped with an UV reactor and a NDIR detector, which measured the content of carbon dioxide generated from oxidation of organic compounds by sodium persulfate to quantify

the concentration of those compounds. Prior to analysis, the concentration of organic compounds in samples was diluted to one-fiftieth to meet the measuring ranges (20.0–1000.0 mg l<sup>-1</sup>), which had been calibrated by the potassium hydrogen phthalate standard solution.

#### 2.4. Gas chromatograph/mass spectrometer analysis (GC/MS)

In proceeding the photo-ozonation experiments, the spent acid sampled was blended with toluene ( $\geq 99.5\%$ , Fluka) in an extractor, as described in our previous report [4], to extract and concentrate 10-fold the reaction intermediates involved in the acid phase. Subsequently, the proportionate amount of toluene (0.3  $\mu$ l), separated from the spent acid, was injected into a gas chromatograph/mass spectrometer (Hewlett-Packard 59864B/HP 5973 MASS) equipped with a capillary column (Metal ULTRA ALLOY UA-5, 30 m  $\times$  0.25 mm, film thickness 0.25  $\mu$ m) operated from 313 to 573 K at a programming rate of 20 K min<sup>-1</sup>. The mass spectra obtained were used to identify the ingredients involved in the extract by comparing those with the authentic standard compounds of database (Wiley 275.L).

#### 2.5. Gas chromatograph/flame ionization detector analysis (GC/FID)

The toluene solution, decanted from the extractor, was further analyzed by a gas chromatograph (Hewlett-Packard 6890 SERIES) equipped with a flame ionization detector. A capillary column (DB-1, 100 m  $\times$  0.25 mm, film thickness 0.5  $\mu$ m, J & W Co.) operated from 373 to 493 K was used to quantify the compositions.

#### 2.6. Pyrolysis/GC/MS analysis

During the course of photo-ozonation testing, the spent acid sampled was situated in the flask immersing in a bath-reciprocal shaker equipped with a cooler (DENG YNG DKW-40 L Model). The temperature of spent acid was refrigerated to 273 K and maintained for 2 h. Subsequently, the spent acid achieved was passed through the micro-filtration system (Gelman Sciences Magnetic Filter) to remove some crystal-like solids, which conducted the Pyrolysis/GC/MS analysis to disclose the ingredients.

### 3. Results and discussion

#### 3.1. Effect of reaction temperature on ozonation

According to the extracting method established in our previous study [4], the TOC involved in spent acid was identified by GC/MS and quantified by GC/FID analyses. Table 1 summarizes the results obtained, wherein the compositions are 78.53% 2,4-DNT; 17.70% 2,6-DNT; 0.40% 2,3-DNT; 1.53% 3,4-DNT and 1.84% 2,4,6-TNT on the weight basis.

Due to sharp reduction of solubility of ozone in water after exceeding 313 K, the reaction temperature chosen was in the range of 288–313 K. Fig. 2 illustrates the residual TOC content

Table 1  
Compositions of TOC in spent acid from toluene nitration process

2,4-DNT (wt.%)	78.53
2,6-DNT (wt.%)	17.70
2,3-DNT (wt.%)	0.40
3,4-DNT (wt.%)	1.53
2,4,6-TNT (wt.%)	1.84

in spent acid treated at different reaction temperature. Apparently, the organic compounds (e.g. DNT isomers and 2,4,6-TNT) were gradually mineralized by ozonation, of which oxidation efficiency was about 78.0% at 313 K after 7 h treatment. It is noteworthy that the residual TOC content at 313 K was less than that of 303 K (1120 mg l<sup>-1</sup> versus 2030 mg l<sup>-1</sup>), whereas the solubility of ozone in water for the former is less than that of the latter (4.2 mg/1000 g versus 7.7 mg/1000 g) [28]. It clearly indicates that the mineralization of organic compounds mainly depends upon the oxidative degradation step, i.e. rate determined step. That reveals the destruction of organic compounds was scarcely contributed by hydroxyl radicals, of which oxidation rate with those compounds is essentially faster than that of ozone alone [29]. Consequently, the phenomenon observed may be interpreted with oxidation of organic compounds by ozone, which would not decompose into hydroxyl radicals. As far as the acidity of spent acid is concerned (pH  $\leq 0$ ), the experimental condition would be unfavorable for the occurrence of ozone decomposition, which is preferable to take place under the pH range of 8.0–10.0 in wastewater treatment [30–33]. Similar outcomes have been also reported by Beltrán et al. [24], who showed the positive effect of reaction temperature on the ozonation rate of 2,6-DNT contained in wastewater.

#### 3.2. Effect of light intensity on photo-ozonation

The combination of ozonation and UV irradiation (254 nm) has been proved to be highly effective for the remediation of

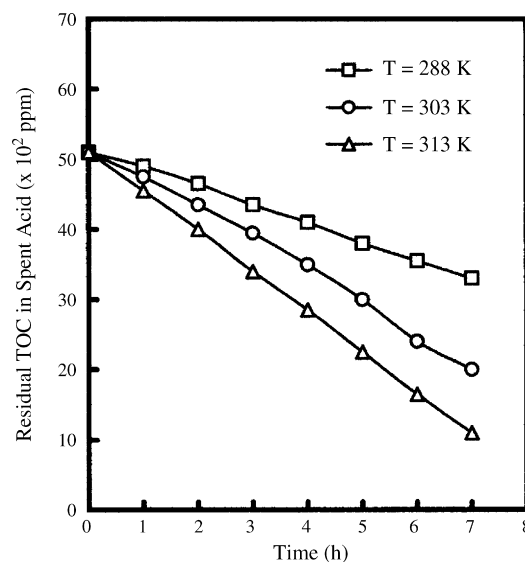


Fig. 2. Effect of reaction temperature on the mineralization of organic compounds in spent acid under the condition of O<sub>3</sub> = 3.8 g h<sup>-1</sup> and atmospheric pressure.

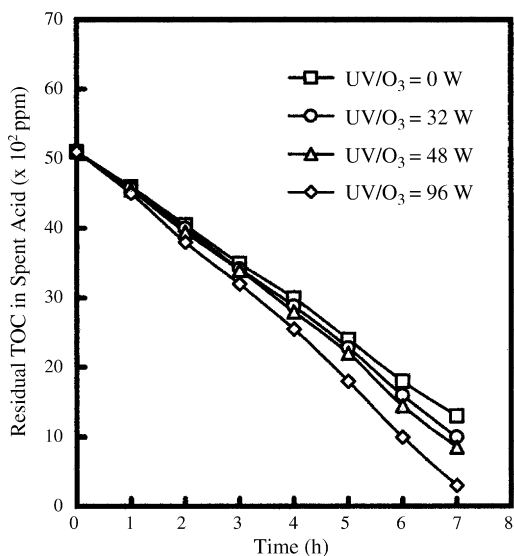
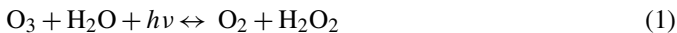


Fig. 3. Effect of intensity of UV irradiation on the mineralization of organic compounds in spent acid under the condition of  $O_3 = 3.8 \text{ g h}^{-1}$  and  $T = 312 \text{ K}$ .

nitroaromatic compounds in wastewater [21,25,34,35]. According to the study by Peyton and Glaze [36], hydroxyl radicals could be generated in water by photo-ozonation (shown as follows), which should result in higher oxidation efficiency of organic compounds in comparison with that of ozone.



In order to enhance the mineralization efficiency of organic compounds, UV/O<sub>3</sub> was also employed to treat DNT isomers and 2,4,6-TNT in spent acid. Effect of UV irradiation intensity on the destruction of organic compounds is demonstrated in Fig. 3. It is obvious that the residual amounts of TOC exhibit a decreasing trend with the increasing light intensity. It reveals that the mineralization of nitroaromatic compounds in spent acid by ozonation has been enhanced by UV irradiation. That is, ozone, hydroxyl radicals and UV irradiation may contribute to the destruction of TOC. Further, it is worth noting that TOC of spent acid could be mineralized to carbon dioxide and water completely under the experimental condition in this study. That implies photo-ozonation method would be directly applied to purification of DNT isomers and 2,4,6-TNT of spent acid in toluene nitration process.

### 3.3. Effect of dosage of ozone on photo-ozonation

To elucidate the role played by UV irradiation, mineralization of TOC in spent acid was conducted using solely UV lamps, i.e.  $O_3 = 0 \text{ g h}^{-1}$  (see Fig. 4). It clearly shows that the organic compounds were gradually destroyed by UV irradiation alone, in agreement with the results reported by several researchers [20,25,37–39]. Additionally, the residual TOC content exhibits a decreasing trend with the increasing dosage of ozone. It is anticipated in accelerating destruction rate of organic compounds with the increasing dosage of ozone. Further, in the absence of ozone, the mineralization efficiency of TOC by UV irradiation

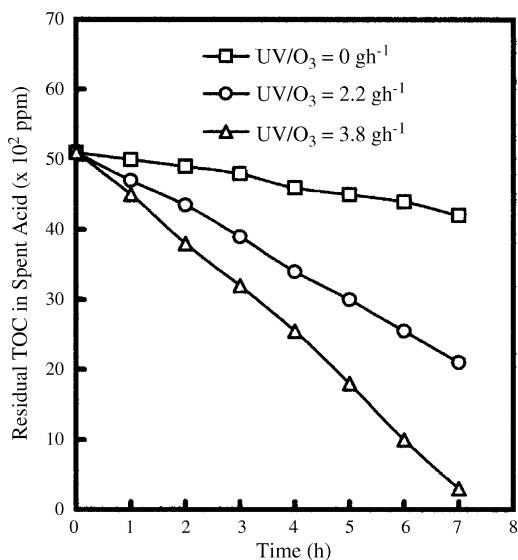


Fig. 4. Effect of dosage of ozone on the mineralization of organic compounds in spent acid under the condition of  $UV = 96 \text{ W}$  and  $T = 312 \text{ K}$ .

is about 17.6%, whereas the value induced by ozonation with UV irradiation reaches a level as high as 94.0%. The increment on the mineralization efficiency of TOC is about 76.4%, which is nearly equivalent to that of ozonation alone (see Fig. 3). Thus, one may deduce that the TOC in spent acid is mineralized by ozonation and UV irradiation, respectively.

As far as dosing amounts of ozone are concerned, the destruction efficiency of organic compounds seems to be independent of solubility of ozone, but depends principally upon oxidation rate. That is, the mineralization of DNT isomers and 2,4,6-TNT was significantly contributed by ozone, of which rate constants in oxidation reactions were far lower than those of hydroxyl radicals [29]. Therefore, it gives another evidence which supports our hypothesis as described in previous paragraph.

For the sake of making clear the oxidizing agent in photo-ozonation, e.g. ozone, hydrogen peroxide and/or hydroxyl radicals, ferrous ion was added into the spent acid. Fig. 5 illustrates the influence of concentrations of ferrous ion on the residual TOC content in spent acid. Obviously, the same value for the mineralization efficiency was found among the tests. According to our previous study with relation to treatment of spent acid [27], hydroxyl radicals would be arisen from Fenton's reagent ( $H_2O_2/Fe^{2+}$ ), of which oxidizing activity is superior to that of ozone or hydrogen peroxide. Thus, the mineralization efficiency of TOC by hydroxyl radicals should be higher than that of ozone or hydrogen peroxide. Additionally, oxidation of ferrous ion into ferric ion by oxygen is proportional to  $[OH^-]^2$  and decreases more sharply with pH than oxidation of ferrous ion by hydrogen peroxide, which is proportional to  $[OH^-]$  [40]. That is, reaction of ferrous ion with hydrogen peroxide would be more dominant in spent acid. Nevertheless, it seems that ozone was hardly converted into hydrogen peroxide and subsequently decomposed into hydroxyl radicals under the condition of photo-ozonation. As a consequence, the result supports our previous inference that the mineralization of DNT isomers and 2,4,6-TNT in spent acid developed through ozone oxidation.

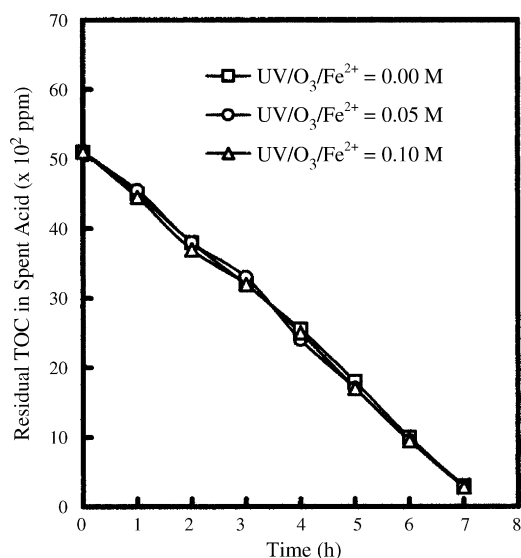


Fig. 5. Effect of dosage of ferrous ion on the mineralization of organic compounds in spent acid under the condition of  $O_3 = 3.8 \text{ g h}^{-1}$ ,  $UV = 96 \text{ W}$  and  $T = 312 \text{ K}$ .

#### 3.4. Effect of concentration of sulfuric acid on photo-ozonation

It has been recognized that hydroxyl radicals could be produced by direct photolysis (254 nm) of ozone in the aqueous solution [25,36]. Due to apparently lower pH value of spent acid ( $\text{pH} \leq 0$ ), the influence of concentration of sulfuric acid on mineralization of DNT isomers and 2,4,6-TNT was investigated to elucidate the oxidation mechanism in photo-ozonation. As illustrated in Fig. 6, no difference in residual TOC content in spent acid was obtained among the sulfuric acid concentration of 50–74 wt.%. Thus, one deduces that in spent acid the destruction of TOC was principally by means of ozone as described

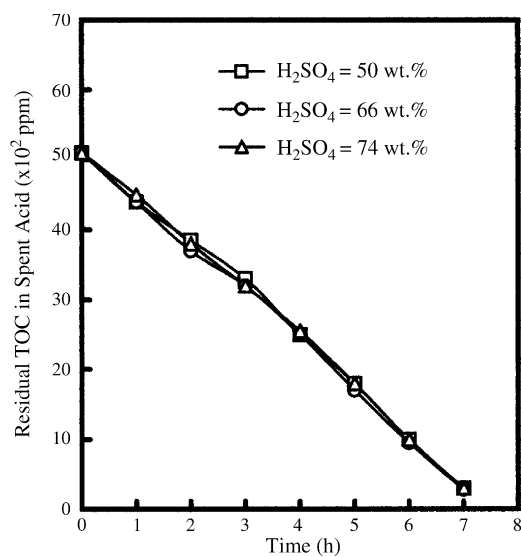


Fig. 6. Effect of concentration of sulfuric acid on the mineralization of organic compounds in spent acid under the condition of  $O_3 = 3.8 \text{ g h}^{-1}$ ,  $UV = 96 \text{ W}$  and  $T = 312 \text{ K}$ .

in previous paragraph. Therefore, ozone would not be decomposed into hydroxyl radicals by UV irradiation in this work. This fact provides another proof on the hypothesis as mentioned. As considering the water molecules shown in Eq. (1), the phenomenon observed might be interpreted with existence of considerable amounts of sulfuric acid molecules, which are bound by water molecules. That led to the absence of free water molecules, which participated in the photo-ozonation.

#### 3.5. Reaction pathways of mineralization of organic compounds by photo-ozonation

In order to disclose the oxidative degradable intermediates involved in photo-ozonation, the samples obtained from toluene extraction of spent acid treated in photo-ozonation were analyzed by GC/MS spectrometer. As shown in Fig. 7(a), there exist five peaks, which have been proved to be *o*-, *m*-, *p*-mononitrotoluene (MNT) for the former three peaks (retention times: 10.88; 11.29; 11.42 min) by means of mass spectra given (see Table 2). The compositions of the extract were further verified by GC/FID analysis. Besides, the spent acid achieved in photo-ozonation was also refrigerated to 273 K for 2 h and

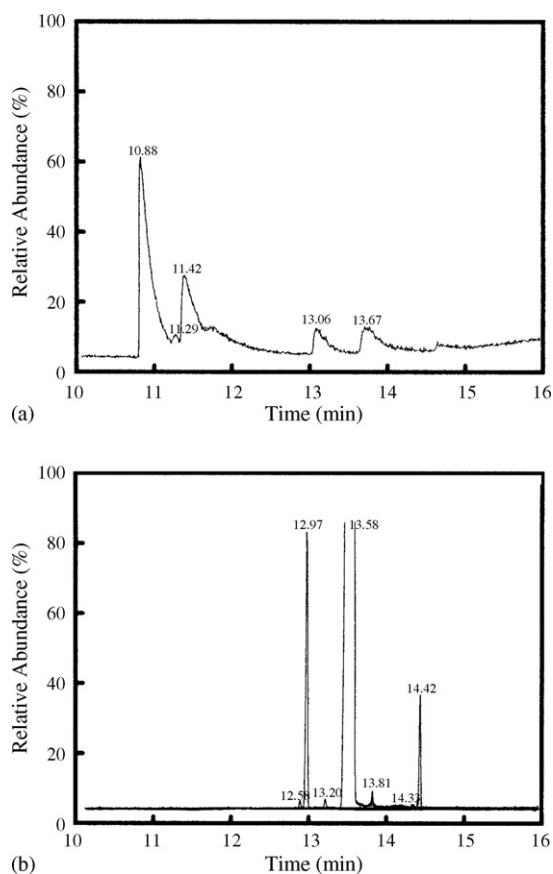


Fig. 7. GC spectra of the sample obtained in photo-ozonation. (a) Toluene extract by GC/MS analysis, retention times: 10.88 min (*o*-MNT), 11.29 min (*m*-MNT), 11.42 min (*p*-MNT); (b) crystal solid by Pyrolysis/GC/MS analysis, retention times: 12.88 min (1,3-DNB), 12.97 min (2,6-DNT), 13.20 min (2,3-DNT), 13.81 min (3,4-DNT), 14.33 min (1,3,5-TNB), 14.42 min (2,4,6-TNT).

Table 2  
Reaction intermediates of photo-ozonation detected and identified by GC/MS and Pyrolysis/GC/MS analyses

Reaction intermediates	Retention time (min)	<i>m/z</i> (relative abundance)
<i>o</i> -MNT	10.88	39(27.1%), 62(28.1%), 65(83.4%), 77(30.2%), 89(31.6%), 91(60.2%), 92(61.5%), 120(100%)
<i>m</i> -MNT	11.29	39(21.2%), 50(10.5%), 62(21.6%), 65(57.2%), 77(12.1%), 89(17.3%), 91(100%), 137(61.5%)
<i>p</i> -MNT	11.42	39(25.0%), 62(26.2%), 65(70.1%), 77(26.2%), 89(20.4%), 91(100%), 107(34.9%), 137(86.0%)
1,3-DNB	12.88	30(48.9%), 51(58.8%), 65(21.9%), 75(75.8%), 77(77.6%), 92(38.8%), 122(31.0%), 168(100%)
2,6-DNT	12.97	62(35.2%), 77(20.2%), 78(16.8%), 89(41.0%), 91(28.0%), 121(17.8%), 148(20.1%), 165(100%)
2,3-DNT	13.20	30(13.5%), 62(33.6%), 65(14.8%), 78(16.6%), 89(50.2%), 90(18.6%), 120(25.8%), 166(100%)
2,4-DNT	13.58	50(13.1%), 62(35.9%), 77(17.3%), 89(60.8%), 90(25.1%), 120(25.8%), 165(100%), 166(14.1%)
3,4-DNT	13.81	30(63.5%), 39(32.2%), 51(32.2%), 62(47.8%), 65(33.9%), 78(46.8%), 89(51.5%), 182(100%)
1,3,5-TNB	14.33	30(44.2%), 62(20.5%), 74(46.8%), 75(100%), 120(28.4%), 166(20.2%), 212(51.5%), 213(51.1%)
2,4,6-TNT	14.42	30(15.5%), 62(17.1%), 63(32.5%), 75(15.2%), 89(43.5%), 180(13.9%), 193(13.5%), 210(100%)

acquired some crystal-like solids, which have been identified to be 1,3-dinitrobenzene (DNB), 2,6-DNT, 2,3-DNT, 2,4-DNT, 3,4-DNT, 1,3,5-trinitrobenzene (TNB) and 2,4,6-TNT by means of Pyrolysis/GC/MS analysis (shown in Fig. 7(b); Table 2). The seven components correspond to the broad peaks observed for the latter two group (retention times: 13.05; 13.67 min) in Fig. 7(a). With respect to the ingredients of 2,4-DNT, 2,6-DNT, 2,3-DNT, 3,4-DNT and 2,4,6-TNT, they may be attributed to the organic compounds feedstock in spent acid, as described in previous report [4]. Nevertheless, the *o*-, *m*-, *p*-MNT may convince us of being reaction intermediates in accordance with their peak areas which are larger than others, whereas DNT isomers are main components in the spent acid feedstock.

It has been well known that the aromatic ring reaction with ozone would be significantly accelerated with electron-donating

group (methyl) and retarded with electron-withdrawing group (nitro). Therefore, it is likely that mononitrotoluenes were oxidized faster than dinitrotoluenes [23]. Thus, based on the relative magnitude of MNT and DNT peaks (referred to Fig. 7(a)), one may deduce that the mononitrotoluenes were derived from dinitrotoluenes, of which methyl group would promote the electron density of nitro groups to be oxidized more readily.

As indicated, there exists a little amount of 1,3-DNB, which may derive from direct oxidation of methyl group in 2,4-DNT or 2,6-DNT and decarboxylation of 2,4- or 2,6-dinitrobenzoic acid subsequently, in agreement with the report by Larson et al. [39]. Consequently, the multiple oxidation pathways of 2,4-DNT in spent acid by photo-ozonation could be demonstrated in Fig. 8. Besides, the mineralization pathway of 2,4,6-TNT may

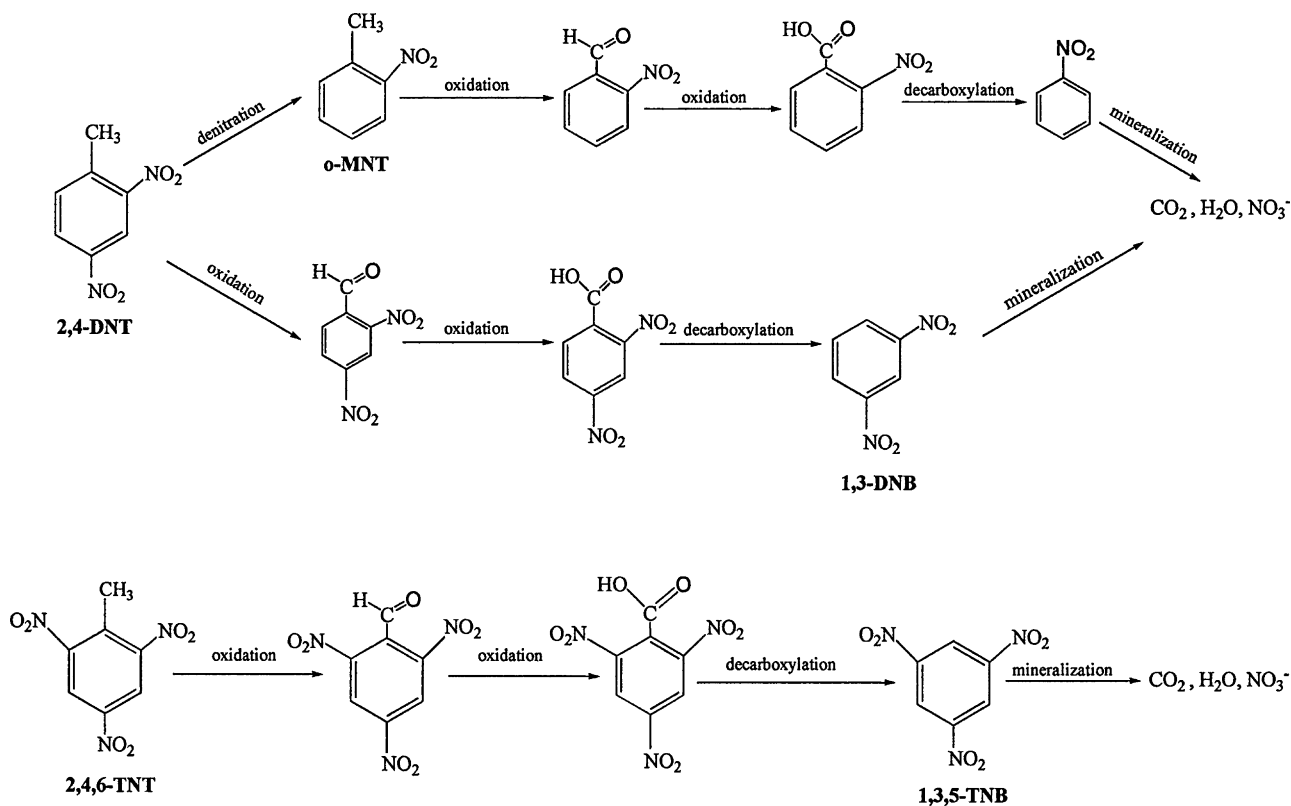


Fig. 8. Plausible reaction pathways of mineralization of organic compounds in spent acid by photo-ozonation.

be proposed as follows on account of presence of 1,3,5-TNB (see Fig. 8). At first, the methyl group of 2,4,6-TNT was oxidized to trinitrobenzaldehyde, which proceeded oxidation into trinitrobenzoic acid. Subsequently, decarboxylation of aromatic acid and mineralization of nitro group on the aromatic ring gave the ultimate products of carbon dioxide, nitrate ion and water.

#### 4. Conclusion

Based on the above discussion, it appears that DNT isomers and 2,4,6-TNT in spent acid from toluene nitration process were mineralized by ozonation and UV irradiation, respectively. Nonetheless, it was found that hydroxyl radicals would not be formed by way of ozone decomposition or photolysis of ozone. In addition, it is remarkable that the nearly complete mineralization of TOC can be achieved by ozonation combined with UV irradiation. It reveals that the method established may be utilized to purify spent acid industrially. According to the spectra identified by GC/MS and Pyrolysis/GC/MS spectrometer, the plausible oxidation pathways of organic compounds by photo-ozonation are suggested as follows. The multiple oxidative degradation of DNT isomers leads to *o*-, *m*-, *p*-mononitrotoluene and 1,3-DNB, respectively. Meanwhile, oxidation of 2,4,6-TNT results in formation of 1,3,5-TNB.

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