

Nitroaromatic Hydrocarbon Ozonation in Water. 1. Single Ozonation

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Single ozonation of two nitroaromatic hydrocarbons (nitrobenzene and 2,6-dinitrotoluene) under different experimental conditions (ozone feed rate, pH, temperature, hydroxyl radical scavengers) has been studied. The absence of hydroxyl radical scavengers, pHs 7–9, and temperatures below 30 °C are optimum conditions for nitroaromatic removal. Due to the importance of hydroxyl radical reactions, removal rates in natural water are much lower than those observed in laboratory ultrapure water. Rate constants of the direct reaction between ozone and nitroaromatic hydrocarbons at 20 °C have been found to be lower than 6 M⁻¹ s⁻¹. More than 99% of nitroaromatic removal is due to hydroxyl radical oxidation. Single ozonation of nitroaromatics can then be classified as a real advanced oxidation technology. Nitrophenols, compounds very reactive toward ozone and hydroxyl radicals, and 2,6-dinitrobenzaldehyde, identified in the single ozonation of nitrobenzene and 2,6-dinitrotoluene, respectively, are some of the first intermediates of single ozonation.

Introduction

Although nitroaromatic hydrocarbons are included in lists of water priority pollutants (Harrison, 1990), there are few research studies about their specific removal from water. Nitroaromatic hydrocarbons are employed as raw materials of many industrial processes such as those for the preparation of pesticides, explosives, textiles, pulp and paper, etc. Consequently, these compounds have been found in water environments as a result of their release in industrial wastewater (Shackelford et al., 1983; Hashimoto et al., 1982). Previous works report the presence of these compounds not only in industrial wastewater but also in surface water and even groundwater with concentrations up to 1.4 mg L⁻¹ (Howard, 1989; Duguet et al., 1990). Like other water pollutants, nitroaromatic hydrocarbons also present adverse effects on human health (King, 1982). Therefore, specific studies on the removal of these compounds from water are advisable.

Both single and combined ozonations (ozone alone or applied together with hydrogen peroxide or UV radiation, respectively) have been shown to be recommended techniques for removal from water priority pollutants like pesticides, volatile organochlorine compounds, polynuclear aromatic hydrocarbons, etc. (Kearney et al., 1987; Hayasi et al., 1993; Glaze and Kang, 1989; Beltrán et al., 1995a, 1996b). The ozonation of some nitroaromatic hydrocarbons has been previously studied by Glaze et al. (1992) and Akata and Gurul (1992) on the removal of nitrobenzene and Guitonneau et al. (1990) on degradation of chloronitrobenzene. The former work reports data on single ozonation and ozone combined with hydrogen peroxide oxidation, while the latter

focuses on the UV/ozone oxidation system. From these works it is deduced that effects of variables like pH, ways of ozone action, or mechanism and kinetics deserve more specific attention.

In this work an extensive study on the water chemical oxidation of two nitroaromatic hydrocarbons, nitrobenzene (NB) and 2,6-dinitrotoluene (DNT), with ozone alone (single ozonation) and combined with hydrogen peroxide or UV radiation (combined ozonation) is presented. The work is divided in three parts dedicated to single ozonation, combined ozonation, and mechanism and kinetic modeling of these processes. This paper is devoted to single ozonation.

Experimental Part

Ozonation reactions were carried out in a 5000 cm³ standard agitated tank similar to that described in detail in a previous work (Beltrán et al., 1995a). The reactor, operated in semibatch mode, was provided with four equally spaced baffles and a stainless steel six blade turbine. The reactor was submerged in a bath where water from a Frigiterm Selecta S-382 thermostatic equipment was recirculated to keep constant the temperature of ozonation (± 0.5 °C).

Nitrobenzene and 2,6-dinitrotoluene (99% purity) were obtained from Aldrich and *tert*-butyl alcohol (>99% purity), used to quench radical reactions during ozonation, was supplied by Merck. Most of aqueous solutions were prepared with ultrapure water of characteristics given previously (Beltrán et al., 1995b) obtained from a Millipore MilliQ system. Surface water from the river Guadiana (Badajoz, Spain) was also used in some runs. This water, filtered before used through 0.4- μ m Millipore membranes, had 15 mg L⁻¹ carbon content, as determined in a 915 Beckman carbon analyzer. Ozone was produced from pure oxygen in a laboratory ozonator at concentrations between 4.2×10^{-5} and 8.3×10^{-4} M.

Analytical determinations were quantitative for nitroaromatic hydrocarbons and ozone and qualitative for

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ozonation byproduct identification. Thus, nitrobenzene and 2,6-dinitrotoluene concentrations were determined by HPLC using a 250-mm length, 4.6-mm i.d. C18 Nucleosil column (100-Å particle size), with a 1050 Hewlett-Packard pump and a 486 Waters variable wavelength detector. Mobile phase was acetonitrile–water (60:40) v/v with 1 mL min⁻¹. Detection was made at 254 nm. Under these conditions retention times for nitrobenzene and 2,6-dinitrotoluene were 7.5 and 7.1 min, respectively. Ozone concentration was analyzed both in water and gas phases (at the reactor inlet and outlet) as indicated in a previous work (Beltrán et al., 1995b). Identification of ozonation intermediates was carried out by GC/MS following the procedure indicated by Beltrán et al. (1996a).

The individual liquid phase mass transfer coefficient was obtained from a procedure described in detail in a previous paper (Beltrán et al., 1994). The coefficient was found to be 2.4×10^{-4} ms⁻¹ for 50 L h⁻¹ gas flow rate and 1000 rpm of agitation speed.

Results and Discussion

Influence of Variables. Variables investigated were initial nitroaromatic concentration [(5×10^{-6}) – (8×10^{-5}) M], ozone feed rate [(3×10^{-5}) – (7×10^{-4}) mol min⁻¹], pH (2–12, phosphoric acid and sodium hydroxide were used for pH adjustment), presence of hydroxyl radical scavengers (10^{-4} – 10^{-1} M *tert*-butyl alcohol), temperature (2–30 °C), and water nature (18 MΩ cm⁻¹ laboratory prepared water and surface water from the river Guadiana (Badajoz, Spain) with 15 mg L⁻¹ TOC).

Previous experiments, where oxygen at 50 L h⁻¹ was passed through the nitroaromatic aqueous solution, shown no evidence that volatilization takes place.

Effect of Initial Nitroaromatic Concentration.

Figure 1 shows the evolution of the remaining concentration of NB and DNT with time for experiments at different initial nitroaromatic concentration. As can be deduced, at a given time, an increase of initial concentration leads to a decrease of nitroaromatic hydrocarbon conversion though the ozonation rate increases. Thus, at 10 min, NB has completely disappeared if starting with a concentration $\leq 5 \times 10^{-6}$ M, while only 20% conversion is reached if the NB initial concentration is about 16 times higher. Initial rates of ozonation are, however, 4.2×10^{-6} and 8×10^{-5} M min⁻¹ for initial concentrations of 5.4×10^{-6} and 8.1×10^{-5} M, respectively. In the case of DNT ozonation results are qualitatively similar although ozonation rates are much lower at similar conditions. It takes 10 and 40 min to remove NB and DNT, respectively, completely from water with an ozone feed rate of 5×10^{-5} mol min⁻¹, the initial nitroaromatic concentration being approximately 5×10^{-6} M. Another important feature of these experiments is the presence of dissolved ozone, which suggests the reactions can be classified as of the slow kinetic regime according to Charpentier (1981).

Given the molecular structure of nitroaromatic hydrocarbons studied, which are characterized by the presence of nitro substituent groups, it is foreseen that direct reactions with ozone contribute little to the ozonation rate. Nitro groups deactivate the electrophilic aromatic substitution reactions, a way through which ozone reacts with aromatic compounds (Bailey, 1958). Accordingly, it is expected that decomposition of nitroaromatic compounds in water with ozone develops through free radical reactions as suggested by Glaze et al. (1992).

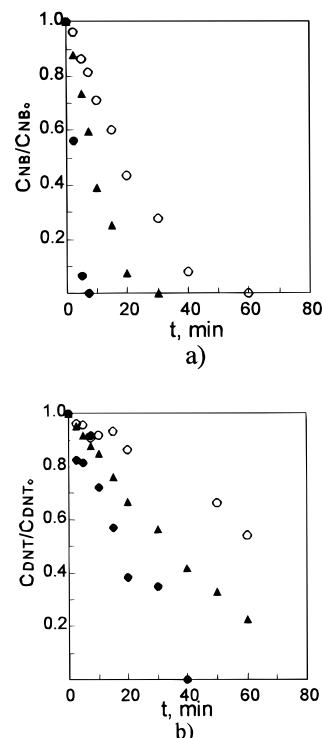


Figure 1. Single ozonation of nitroaromatic hydrocarbons. Influence of initial hydrocarbon concentration. Conditions: $T = 20$ °C, pH 7; $m_e = 5.5 \times 10^{-5}$ mol min⁻¹ (150 Pa, average value). (a) NB ozonation: $C_{NB,0} \times 10^5$, M: ● 0.5; ▲ 5.7; ○ 8.1. (b) DNT ozonation: $C_{DNT,0} \times 10^5$, M: ● 0.5; ▲ 5.3; ○ 7.0.

Effect of Ozone Rate. Figure 2 presents the variation of the remaining concentration of NB and DNT with time corresponding to ozonation runs at different ozone feed rates. As can be observed, the increase of ozone feed rate leads to an increase of both ozonation rate and nitroaromatic hydrocarbon conversion at a given time. The increase of ozonation rate is likely due to the increase of ozone concentration driving force. Ozonation rates are much lower than those found for polynuclear aromatic hydrocarbons (Beltrán et al., 1995a) or phenols (Sotelo et al., 1990), which supports the idea that the presence of nitro groups deactivates the direct reaction with ozone. Comparing the ozonation of both nitroaromatic compounds, if direct ozonation or direct ozone-compound reaction is negligible (see later), nitro groups also contribute to deactivating reactions with hydroxyl radicals since the removal rates of DNT are much lower than those of NB.

Another point of interest is the evolution of ozone gas concentration at the reactor outlet as presented in Figure 3 for the case of NB ozonation. It is observed that ozone concentration increases with time to reach two consecutive plateau values. The first one terminates approximately at a time when the initial nitroaromatic hydrocarbon disappears. This confirms that some changes in the reactivity are taking place. Thus, the increase of ozone concentration once nitroaromatic hydrocarbons have disappeared suggests that reactions of ozone are even slower than those corresponding to the initial period in the presence of NB or DNT. This is in accordance with the mechanism proposed by Decorret et al. (1984) on the ozonation of aromatics.

Effect of Temperature. Temperature had a positive effect on the ozonation rate of compounds studied, except for the case of NB at 30 °C. Thus, in a 40 min reaction, conversion of NB is 60 and 40% at 20 and 30

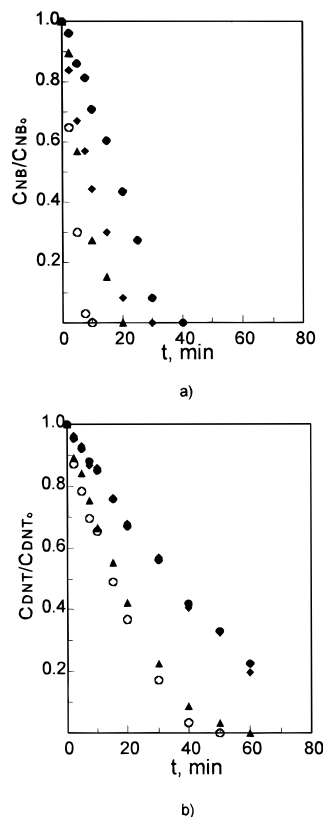


Figure 2. Single ozonation of nitroaromatic hydrocarbons. Influence of ozone feed rate. Conditions: $T = 20^\circ\text{C}$, $\text{pH} = 7$. (a) NB ozonation. $C_{NB_0} = 8 \times 10^{-5}$ M (average). $m_e \times 10^5$, mol min⁻¹: ● 4.86; ◆ 9.00; ▲ 18.03; ○ 30.88. (b) DNT ozonation. $C_{DNT_0} = 4.5 \times 10^{-5}$ M (average). $m_e \times 10^5$, mol min⁻¹: ● 5.54; ◆ 8.66; ▲ 18.72; ○ 36.76.

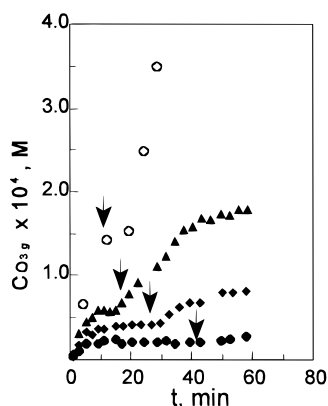


Figure 3. Single ozonation of nitroaromatic hydrocarbons. Influence of ozone feed rate. Evolution of ozone concentration in the gas at the reactor outlet. Conditions: $T = 20^\circ\text{C}$, $\text{pH} 7$. $C_{NB_0} = 8 \times 10^{-5}$ M (average). $m_e \times 10^5$, mol min⁻¹: ● 4.86; ◆ 9.00; ▲ 18.03; ○ 30.88. Vertical arrows indicate time when NB disappears.

$^\circ\text{C}$, respectively, with 6.8 mol min^{-1} of ozone in the feed gas. It seems that at this level of temperature, the negative effect of temperature on ozone solubility is crucial to improve the ozonation rate. This effect has also been observed in the ozonation of other compounds like mecoprope (Beltrán et al., 1994). For practical purposes it is then recommended to keep ozonation temperature below 30°C .

Effect of pH. Due to the catalytic action of hydroxyl ions on the ozone decomposition (Staehelin and Hoigné, 1985) and the possible importance of radical reactions in the ozonation of nitroaromatic hydrocarbons, pH is

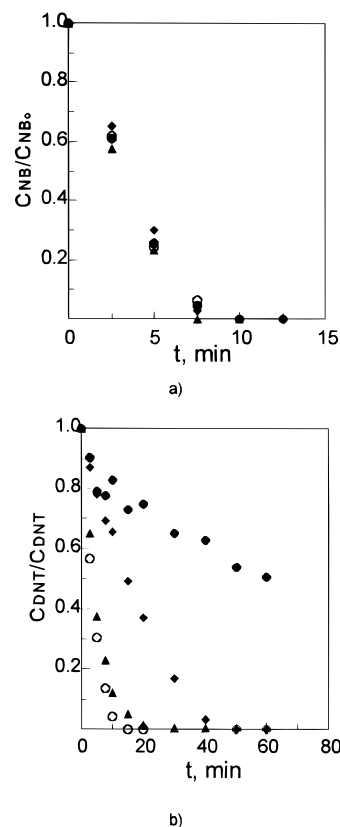


Figure 4. Single ozonation of nitroaromatic hydrocarbons. Influence of pH. Conditions: $T = 20^\circ\text{C}$. (a) NB ozonation. $C_{NB_0} = 6 \times 10^{-5}$ M. $m_e = 3.57 \times 10^{-4}$ mol min⁻¹ (average values). pH: ● 2; ◆ 7; ▲ 9; ○ 12. (b) DNT ozonation. $C_{DNT_0} = 4.65 \times 10^{-5}$ M. $m_e = 3.77 \times 10^{-4}$ mol min⁻¹ (average values). pH: ● 2; ◆ 7; ▲ 9; ○ 12.

probably the main variable in this study. Figure 4 presents the results obtained during the ozonation of NB and DNT at different pHs and 3.4×10^{-4} mol min⁻¹ ozone feed rate (approximately 1% by volume). As can be seen from Figure 4 trends of concentrations with time are different depending on nitroaromatic hydrocarbon. Thus, from Figure 4b, the case of DNT ozonation, a positive effect of pH between 2 and 12 is observed, although differences between pH 9 and 12 are slight. In the case of NB (Figure 4a), however, differences of remaining concentration with pH are rather small and at pH 12 the process seems to be partially inhibited. Since nitroaromatic hydrocarbons are nondissociating compounds, the rate constant of their direct reaction with ozone is independent of pH. Thus, from Figure 4a it can be deduced that NB also decomposes through direct reaction with ozone. However, when the effect of pH was studied at a lower ozone feed rate (5.1×10^{-5} mol min⁻¹) removal rates of NB at pH 2 and 7 were quite different (i.e., at 20-min reaction, 30 and 60% NB conversions were achieved at pH 2 and 7, respectively). This again supports the importance of free radical reactions. Inhibition at pH 12 could be due to the dissociation of hydroxyl radicals into the oxygen anion radical through the equilibrium (Buxton et al., 1988):



Since the $\text{p}K$ is 11.9, equilibrium (1) is shifted to the right at $\text{pH} > 12$. On the other hand, the fast ozonation rate at pH 2 (Figure 4a) suggests the presence of compounds promoting the decomposition of ozone through reactions yielding free radicals able either to regenerate

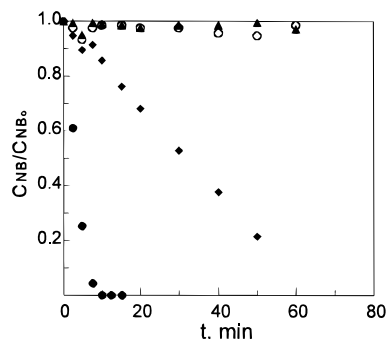


Figure 5. Single ozonation of nitrobenzene. Influence of *tert*-butyl alcohol concentration. Conditions. $T = 20\text{ }^{\circ}\text{C}$, pH 2. $C_{\text{NB}_0} = 9.86 \times 10^{-5}\text{ M}$. $m_e = 3.95 \times 10^{-4}\text{ mol min}^{-1}$ (average values). *tert*-Butyl alcohol concentration, M: \bullet 0; \blacklozenge 1.2×10^{-4} ; \blacktriangle 1.0×10^{-3} ; \circ 1×10^{-1} .

the hydroxyl radical or to produce peroxy radicals reactive with nitroaromatic hydrocarbons (Staehelin and Hoigné, 1985). These compounds could be nitrophenols that react very fast with ozone (Beltrán et al., 1992) and that were identified in this work during the ozonation of NB (see later). According to these results ozonation of nitroaromatic hydrocarbons should be carried out at pH between 7 and 9 to improve the ozonation rates.

Effect of Hydroxyl Radical Scavengers. A series of experiments at pH 2 were carried out in the presence of *tert*-butyl alcohol, a compound that reacts very slowly with ozone (the rate constant of the direct *tert*-butyl alcohol–ozone reaction has been reported to be $0.03\text{ M}^{-1}\text{ s}^{-1}$ by Hoigné and Bader, 1983). On the contrary, it is known that *tert*-butyl alcohol reacts with hydroxyl radicals to yield inactive products that terminate the free radical mechanism (Staehelin and Hoigné, 1985). These experiments were carried out at pH 2 to reduce as much as possible contributions of radical reactions. The effect of *tert*-butyl alcohol on the ozonation of NB is shown in Figure 5. It can be observed that the increase of *tert*-butyl alcohol concentration really inhibits the ozonation rate. From Figure 5 it is seen that concentration of NB remains constant with time during single ozonation for a concentration of *tert*-butyl alcohol $\geq 10^{-3}\text{ M}$ (similar results were observed during the single ozonation of DNT under the same experimental conditions). If the evolution of aqueous ozone concentration is followed in these experiments (Figure 6), it is observed that the increase of *tert*-butyl alcohol concentration up to 10^{-3} M leads to a stabilization of ozone concentration in water. The increase of ozone concentration when *tert*-butyl alcohol concentration is also increased could be due to two possible facts: (a) the decomposition reaction of ozone due to hydroxyl radicals is blocked since these radicals will react preferentially with *tert*-butyl alcohol and (b) since the mass transfer coefficient, $k_L a$, also increases as reported by Gurol and Nekouinaini (1985) the ozone absorption rate is higher and the amount of available ozone in water is greater. However, a further increase of *tert*-butyl alcohol concentration up to 0.1 M leads to a decrease of ozone concentration. At this high *tert*-butyl alcohol concentration Gurol and Nekouinaini (1985) have reported up to a 3-fold increase of $k_L a$ so that the ozone concentration should be even higher than that observed in the presence of a lower *tert*-butyl alcohol concentration. It seems evident that in this latter case ozone reacts directly with

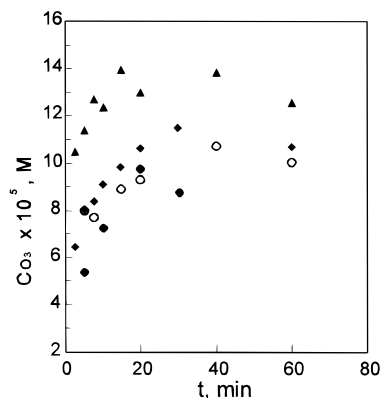


Figure 6. Single ozonation of nitrobenzene. Influence of *tert*-butyl alcohol concentration. Variation of dissolved ozone concentration with time. Conditions. $T = 20\text{ }^{\circ}\text{C}$, pH 2. $C_{\text{NB}_0} = 9.86 \times 10^{-5}\text{ M}$. $m_e = 3.95 \times 10^{-4}\text{ mol min}^{-1}$ (average values). *tert*-Butyl alcohol concentration, M: \bullet 0; \blacklozenge 1.2×10^{-4} ; \blacktriangle 1.0×10^{-3} ; \circ 1×10^{-1} .

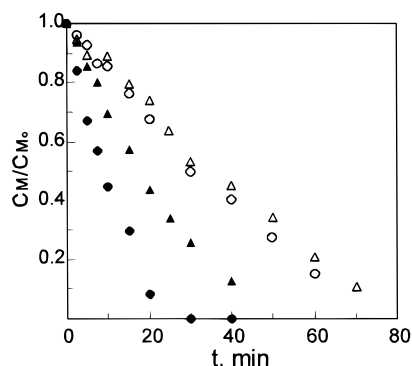


Figure 7. Single ozonation of nitroaromatic hydrocarbons. Influence of water type. Conditions. $T = 20\text{ }^{\circ}\text{C}$. NB ozonation: $C_{\text{NB}_0} = 8.8 \times 10^{-5}\text{ M}$; $m_e = 8.83 \times 10^{-5}\text{ mol min}^{-1}$ (average values). Water type: \bullet ultrapure water (pH 7); \blacktriangle surface water (pH 8). DNT ozonation: $C_{\text{DNT}_0} = 4.65 \times 10^{-5}\text{ M}$; $m_e = 8.32 \times 10^{-5}\text{ mol min}^{-1}$ (average values). Water type: \circ ultrapure water (pH 7); \triangle surface water (pH 8).

tert-butyl alcohol in spite of the very low reaction rate constant.

The effect of hydroxyl radical scavengers was also confirmed in experiments of single ozonation in the presence of carbonate ion (0.1 M) at pH 9 and 12 (not shown). These results are important in a practical case because natural waters contain carbonates that would retard the ozonation rate of nitroaromatic hydrocarbons since ozonation develops through hydroxyl radical reactions. At pH 12 NB is completely removed in less than 10 min at an ozone feed rate of $3.4 \times 10^{-4}\text{ mol min}^{-1}$. In the presence of carbonates, 60-min reactions are needed to reach 80% NB conversion under similar conditions. Results were similar for the case of DNT single ozonation.

Effect of Water Type. Figure 7 presents as example some results obtained during the single ozonation of NB and DNT in ultrapure and surface (river Guadiana) waters. As can be observed from Figure 7 the ozonation rate of nitroaromatic hydrocarbons in ultrapure water is faster than in surface water, likely due to the presence of natural hydroxyl radical scavengers like carbonates, humic substances, etc. From Figure 7 it is also seen that NB needs approximately 25 and 50 min to be completely removed by single ozonation from ultrapure and surface waters, respectively. In the case of DNT the effect of water nature is also evident, though differences were less important.

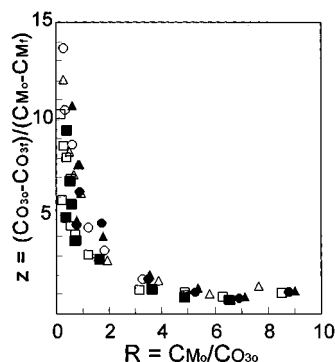


Figure 8. Single ozonation of nitroaromatic hydrocarbons. Determination of direct ozone–nitroaromatic hydrocarbon reaction stoichiometry (eq 5) at different pH. Initial concentration ranges in M: for ozone, (7.4×10^{-6}) – (1.40×10^{-4}) ; for nitroaromatics, (1.99×10^{-5}) – (8.30×10^{-5}) . Open symbols correspond to NB–ozone reaction. Black symbols correspond to DNT–ozone reaction. \circ pH 2; \square pH 7; \triangle pH 9.

Kinetics of Nitroaromatic Hydrocarbon Direct Ozonation. From the analysis of variables it can be concluded that ozonation of nitroaromatic hydrocarbons mainly develops through radical reactions. However, to quantify the importance of direct and indirect or free radical reactions of ozone it is advisable to determine the rate constants of both reactions.

The removal rate of nonvolatile organic compounds in a semibatch aqueous ozonation process is given by eq (2):

$$-(dC_M/dt) = r_D + r_R = k_D C_M C_{O_3} + k_{OHM} C_M C_{OH} \quad (2)$$

where members of the right side of eq 2 represent the contribution of direct ozonation and hydroxyl radical oxidation to the disappearance rate of M. In this study direct reaction of ozone and NB or DNT is assumed to be of second order (first order with respect to ozone and M following the work of Kuczkowski, 1987). For the case of r_R , the second order is evident since this term represents the reaction rate of an elementary step between the hydroxyl radical and M in the mechanism of radical oxidation (Beltrán et al., 1996b). Thus, in eq 2 k_D and k_{OHM} are the rate constants of the reactions. Direct reaction:



Free radical reaction:



In reaction 3 z is the stoichiometric coefficient that was determined by mixing aqueous solutions of ozone and NB or DNT of known concentrations. After a few minutes, remaining concentration of both reactants was analyzed and z obtained according to eq 5:

$$z = \frac{C_{O_{30}} - C_{O_{3f}}}{C_{M_0} - C_{M_f}} \quad (5)$$

Figure 8 shows the evolution of z , calculated from eq 5, with the ratio between initial concentrations of nitroaromatic hydrocarbon and ozone, R . It is observed that z decreases with the increase of R until a plateau value, which was taken as the actual stoichiometric coefficient of reaction 3. It seems evident that at low

values of R ozone is consumed by secondary reactions in addition to reaction 3. When the initial concentration of the hydrocarbon is at least six times higher than that of ozone, reaction 3 is the only way ozone disappears. Thus, from Figure 8 it is deduced that z is 1 mol of ozone consumed per mol of nitroaromatic hydrocarbon consumed.

In eq 2 the main problem in determining k_D is that k_{OHM} and C_{OH} are unknown. Although k_{OHM} can be obtained by other methods (Glaze and Kang, 1989), it is difficult to estimate with accuracy C_{OH} . Thus, k_D could be obtained from ozonation results under conditions where free radical reactions do not develop. This is usually achieved at acid pH, but in the case of nitroaromatic hydrocarbons (see Figure 4) the presence of hydroxyl radical scavengers is also necessary. As shown above, concentrations of *tert*-butyl alcohol higher than 10^{-3} M inhibit the ozonation rate, which suggests that the rate constant of the direct reaction ozone–M is very low. This also allows the determination of k_D from batch ozonation runs where the concentration of ozone can be followed more accurately. In fact, determination of aqueous ozone concentration presents difficulties due to interferences of bubbles when sampling. Accordingly, batch ozonation reactions of NB and DNT at pH 2 in the presence of *tert*-butyl alcohol (10^{-3} M) were carried out. Under these conditions, free radical reaction (4) and reaction of ozone with *tert*-butyl alcohol can be disregarded. In these experiments the initial concentration of nitroaromatic hydrocarbons was more than eight times higher than that of ozone and it remained practically constant with time. Thus, the kinetics was followed by determining the concentration of ozone with reaction time. Hence, the rate of ozone disappearance is

$$-(dC_{O_3}/dt) = r_D = k_D C_M C_{O_3} = k_T C_{O_3} \quad (6)$$

Integration of eq 6 yields

$$\ln(C_{O_3}/C_{O_{30}}) = k_D C_{M_0} t = k_T t \quad (7)$$

Equation 7 was checked with the experimental results of batch ozonations above mentioned (see Figure 9). From Figure 9 it is seen that by plotting $\ln(C_{O_3}/C_{O_{30}})$ versus time experimental points are situated around straight lines whose slopes increase with increasing temperature as expected. Least squares analysis leads to values of slopes and after applying eq 7 to k_D . Results are presented in Table 1. As can be deduced from Table 1, under similar experimental conditions, ozone would react directly with DNT twice as likely as with NB. The higher reactivity of DNT with ozone is likely due to the presence of a methyl group, which activates the electrophilic aromatic substitution reaction (Morrison and Boyd, 1983), the most probable way of ozone direct attack (Bailey, 1958). Rate constants presented in Table 1 were related to temperature with the following Arrhenius equations: For ozone–NB direct reaction,

$$k_D = (259 \pm 10) \exp(-(1403 \pm 40)/T), \text{ M}^{-1} \text{ s}^{-1} \quad (8)$$

For ozone–DNT direct reaction,

$$k_D = ((1.2 \pm 0.1) \times 10^6) \exp(-(3604 \pm 182)/T), \text{ M}^{-1} \text{ s}^{-1} \quad (9)$$

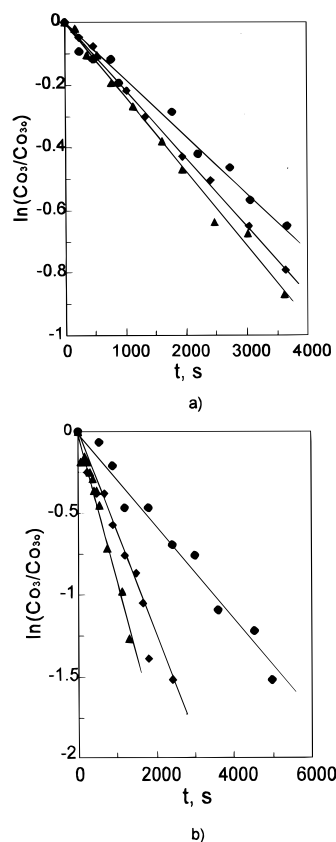


Figure 9. Verification of eq 7. Determination of direct rate constant of ozone–nitroaromatic hydrocarbon reaction. Conditions: batch ozonations, pH 2, *tert*-butyl alcohol concentration = 10^{-3} M. (a) NB ozonation: ● $C_{NB_0} = 1.12 \times 10^{-4}$ M, $C_{O_{3e}} = 9.7 \times 10^{-6}$ M, 2 °C; ◆ $C_{NB_0} = 1.19 \times 10^{-4}$ M, $C_{O_{3e}} = 8.85 \times 10^{-6}$ M, 10 °C; ▲ $C_{NB_0} = 1.08 \times 10^{-4}$ M, $C_{O_{3e}} = 1.3 \times 10^{-5}$ M, 20 °C. (b) DNT ozonation: ● $C_{DNT_0} = 1.19 \times 10^{-4}$ M, $C_{O_{3e}} = 7.8 \times 10^{-6}$ M, 2 °C; ◆ $C_{DNT_0} = 1.40 \times 10^{-4}$ M, $C_{O_{3e}} = 7.8 \times 10^{-6}$ M, 10 °C. ▲ $C_{DNT_0} = 9.24 \times 10^{-5}$ M, $C_{O_{3e}} = 8.96 \times 10^{-6}$ M, 20 °C.

Table 1. Rate Constants of the Direct Reaction between Ozone and Nitroaromatic Hydrocarbons Studied

NB–ozone reaction		DNT–ozone reaction	
$T, ^\circ\text{C}$	$k_D, \text{M}^{-1} \text{s}^{-1}$	$T, ^\circ\text{C}$	$k_D, \text{M}^{-1} \text{s}^{-1}$
2	1.6 ± 0.1	2	2.5 ± 0.2
10	1.8 ± 0.2	10	3.5 ± 0.4
20	2.2 ± 0.2	20	5.7 ± 0.6

^a Values from triplicate batch ozonation experiments at pH 2 with 10^{-3} M *tert*-butyl alcohol.

Since values of k_D are very low, it is deduced that ozonation of nitroaromatic hydrocarbons studied develops through free radical oxidation. In other words, single ozonation is an advanced oxidation in this case (Glaze et al., 1987). This is demonstrated after calculating the contribution of direct reaction, γ_{O_3} , in the total oxidation rate given by eq 2:

$$\gamma_{O_3} = \frac{k_D C_{O_3} C_M}{(dC_M/dt)} \quad (10)$$

Application of eq 10 together with values of k_D leads to γ_{O_3} values lower than 1% regardless of conditions and nitroaromatic hydrocarbon. As a consequence, removal of NB or DNT from water during ozonation processes can be improved by enhancing the formation of hydroxyl radicals, which could be done by combining ozone with

Table 2. Products Detected or Identified during Single Ozonation of Nitrobenzene and 2,6-Dinitrotoluene

product	rt ^a	m/z (relative abundance)
benzaldehyde ^b	14.59	77 (82), 51 (100), 50 (54), 30 (60)
2-nitrophenol ^b	16.46	139 (100), 77 (96), 65 (69)
phthalic anhydride ^b	24.23	148 (19), 104 (100), 76 (92), 74 (23), 50 (58)
unidentified ^b	37.70	149 (100), 29 (30), 27 (63)
unidentified ^b	42.41	150 (9), 149 (100), 76 (7), 29 (16)
unidentified ^b	42.73	149 (100), 76 (13), 41 (31), 29 (35)
unidentified ^b	13.46	89 (50), 63 (100), 46 (63)
unidentified ^b	16.92	89 (59), 63 (100), 51 (52)
2,6-dinitrobenzaldehyde ^c	20.29	92 (39), 75 (100), 50 (40), 30 (43)

^a Retention time in minutes. ^b From NB single ozonation. ^c From DNT single ozonation.

hydrogen peroxide or UV radiation (see also, Beltrán et al., 1997).

Identification of Intermediates. As a complementary part of this work, some ozonated samples were analyzed by GC/MS to identify intermediate products of ozonation. In these analysis, however, most of substances were only detected as shown in Table 2. The most noticeable fact is the presence of 2-nitrophenol. It seems that hydroxyl radicals react with nitrobenzene by means of addition reactions (Hoigné, 1982) as first steps of the mechanism. If nitrophenol is formed it is reasonable to assume that at more advanced reaction times unsaturated carboxylic acids or aldehydes could be among the intermediate and final products as reported by Decoret et al. (1984) in the ozonation of phenols. In this work no acids were identified which comports the fact that the drop in pH during ozonation was less than one possibly because ozonation runs were stopped just after complete disappearance of the nitroaromatic hydrocarbon was noticed. In the case of DNT ozonation, 2,6-dinitrobenzaldehyde was identified, which indicates the oxidation also takes place at the methyl group. Due to the unknown nature of most of the products detected, it is not possible to suggest any probable mechanism. It should be highlighted, however, that once nitrophenols are formed, a possible mechanism of reactions would be that of phenol ozonation (Decoret et al., 1984). In any case, although the nature of intermediates is important, establishment of the molecular reactions of the ozonation mechanism is beyond the scope of the work.

Conclusions

Ozonation of nitrobenzene and 2,6-dinitrotoluene, model compounds of nitroaromatic hydrocarbons, can be readily accomplished with ozone in less than 10 min at 5.1×10^{-5} mol min⁻¹ ozone feed rate. Optimum conditions for ozonation seem to be neutral or weakly basic pH and temperatures between 10 and 30 °C.

Rate constants of the direct reaction between ozone and NB or DNT are below $6 \text{ M}^{-1} \text{ s}^{-1}$, which indicates the process develops through free radical reactions. Consequently, substances that promote or initiate the ozone decomposition in hydroxyl radicals are, at first sight, recommended to accelerate the oxidation rate. On the contrary, scavengers of hydroxyl radicals like the carbonate ion have a negative effect because they quench the oxidation rate by competing for hydroxyl radicals.

In the ozonation of nitrobenzene, nitrophenols were identified. Hence, ozonation of nitrobenzene should be

similar to that reported for phenols (Decoret et al., 1984). It is possible that the high ozonation rates observed at low pH are due to the formation of hydroxyl or organic peroxy radicals from nitrophenols, which react very fast with both ozone and hydroxyl radicals (Beltrán et al., 1992; Buxton et al., 1988).

This work is continued with the combined ozonation (O_3/H_2O_2 and O_3/UV) of NB and DNT and the study of the kinetic modeling of these ozonations as is presented in the next paper (Beltrán et al., 1998) and a forthcoming publication, respectively.

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