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Radiation-Induced Reactions of 2,4,6-Trinitrotoluene in Aqueous Solution

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Radiolysis of aqueous solutions of TNT was examined to provide fundamental information concerning the reactions of TNT with radical species in water. γ-Radiation was used in conjunction with radical scavengers to compare yields for radiation-induced TNT transformation under oxidizing and reducing conditions and in the presence and absence of oxygen. Pulse radiolytic techniques were employed to determine rate constants and absorption spectra for the reactions of TNT with the hydroxyl radical and the aqueous electron. TNT was rapidly transformed under both reducing (1% *tert*-butyl alcohol, N_2 sparged) and oxidizing (N_2O sparged) conditions although rates under reducing conditions were greater. The initial yield for transformation of a 350 μmol L^{-1} TNT solution under reducing conditions was 0.14 μmol/J as opposed to 0.10 μmol/J measured in oxidizing conditions. The reactions of TNT with reduced oxygen species were found to be highly inefficient in aqueous solution. Although TNT is transformed by both oxidizing and reducing radicals, TNT degradation yields in the absence of a radical scavenger were low, indicating that under these conditions there were significant secondary reactions in which the species resulting from reactions between TNT and the primary radicals further reacted to reform the parent compound. The bimolecular rate constant for the reaction between TNT and $^{\bullet}OH$ was determined to be 4.3×10^8 mol^{-1} s^{-1}. Byproduct analyses from γ-radiolysis suggest that hydroxyl radical abstraction of a methyl hydrogen to form the trinitrotoluyl radical is an initial oxidative reaction. The bimolecular rate constant for the reaction between TNT and e_{aq}^- was measured as 3.5×10^{10} mol^{-1} s^{-1}. These results provide quantitative and qualitative insight into the reactions between TNT and the various aqueous radicals produced in many remediation processes.

Introduction

The secondary explosive TNT (2,4,6-trinitrotoluene) is a prevalent contaminant in water, sediment, and soil at many sites where manufacture or demilitarization of munitions was performed (*1, 2*). Certain efforts to degrade TNT in water for purposes of environmental remediation have focused on the use of processes which rely on the generation of aqueous radicals. Such processes include UV/ozone/peroxide combinations (*3*−*6*) and photocatalysis using TiO_2 (*7*−*11*). This situation has created interest in the reactions of TNT with radical species formed in water. However, although TNT has been shown to readily undergo both oxidative and reductive transformations (*12*), few studies have examined relative reaction rates of TNT with different types of radicals. Moreover, rate constants for the reactions of TNT with the primary radicals formed from water are, to the best of the authors' knowledge, currently unavailable in the literature.

Radiolysis has been shown to be an effective technique for elucidating radical reaction mechanisms and rates. The interaction of water with ionizing radiation, such as γ-rays or a high energy electron beam, results in the formation of a suite of radical species in which hydroxyl radicals ($^{\bullet}OH$) and hydrated electrons (e_{aq}^-) are predominant. Through the use of selective scavengers, the reactions of a solute in dilute aqueous solution with these radicals can be investigated. In the current study, radiolysis of aqueous solutions of TNT has been examined. γ-Radiation has been utilized in conjunction with radical scavengers to compare yields for radiation-induced TNT transformation under oxidizing and reducing conditions and in the presence and absence of oxygen. Pulse radiolytic techniques have been employed to determine rate constants and absorption spectra for the reactions of TNT with the hydroxyl radical and the aqueous electron. These data are intended to fill a current gap in the literature by providing fundamental information concerning the reactions of TNT with radical species in water and, thereby, facilitate the application of remediation technologies to TNT contaminated sites.

Experimental Section

Chemicals. The 2,4,6-trinitrotoluene used for experimental work was purchased from Chemservice (West Chester, PA). 3,5-Dinitroaniline was purchased from Aldrich (Milwaukee, WI). Certified standards of 2,4,6-trinitrotoluene, 1,3,5-trinitrobenzene, 2-amino-4,6- dinitrotoluene, 4-amino-2,6-dinitrotoluene, 2,4-dinitrotoluene, and 2,6-dinitrotoluene were purchased from AccuStandard Inc. (New Haven, CT) and were used for identification and quantification. All compounds were of the highest purity available from these vendors and were used without further purification. *tert*-Butyl alcohol (Fisher) was used as a radical scavenger. Nitrogen and oxygen gases were ultrahigh purity, and nitrous oxide was U. S. P. grade. The water used in all experiments and analyses was ultrapure (18 MΩ·cm) prepared using a Milli-Q purification system.

γ-Radiolysis. γ-Radiolysis was carried out with a Shepherd 109 ^{60}Co source. The Shepherd 109 is a concentric well-type source which had an average dose rate of 67.7 Gy/min during the period in which the experiments were conducted. Solutions for γ-irradiation were prepared by mixing reagents with a 220 μmol L^{-1} TNT stock solution which was then saturated with either N_2, O_2, or N_2O by sparging for 90 min. HPLC sample vials of 5 mL were filled with the solutions and sealed with gastight PTFE septa. Sealed vials were then wrapped in paraffin film to further inhibit gas transfer between the solution and the atmosphere.

Pulse Radiolysis. Pulse radiolysis experiments were performed using the linear accelerator at the Notre Dame Radiation Laboratory. The accelerator had an output of 1−5

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Gy/pulse. Absorbance-time profiles at various wavelengths were recorded immediately after pulsing aqueous solutions of TNT. Solutions used to examine hydroxyl radical attack were saturated with N_2O while solutions utilized to analyze reductive attack contained 1% *tert*-butyl alcohol and were deaerated using N_2 gas. The measured absorbance values were calibrated against the extinction coefficient of the thiocyanate radical at 472 nm (7580 L mol^{-1} cm^{-1}). All pulse radiolysis experiments were conducted at neutral pH.

Analysis. Analyses for TNT concentration and intermediate species were made using a Waters HPLC (712 WISP, 600E pump, 996 PDA). The column was a Supelcosil RP-C18 and the eluant was methanol:25 mmol of phosphate buffer (pH = 3.5) in an isocratic ratio of 40:60. Absorbance was measured from 215 to 600 nm using the PDA detector. Intermediate species were identified in all cases by matching both HPLC retention time and absorbance spectra with that of standards.

Results and Discussion

γ-Radiolysis. γ-Radiolysis was used in this work to generate radical species in water. Primary radical and molecular yields resulting from irradiation of water with pH 3−13 by low linear energy transfer (LET) radiation, such as fast electrons and γ-rays, are given in eq 1 (*13*):

$$g(e_{aq}^{-}) = g(^{\bullet}OH) = g(H_3O^{+}) = 0.28;\ g(H) = 0.062;\ g(H_2) = 0.047;\ g(H_2O_2) = 0.072\ (\mu mol/J) \quad (1)$$

When molecular oxygen is present, it reacts rapidly with the aqueous electron and the hydrogen atom to form the superoxide radical anion, O_2^-, and hydroperoxy radical, HO_2. Nitrous oxide also readily scavenges aqueous electrons, forming nitrogen gas and the hydroxyl radical (see eq 2). Consequently, saturation of a solution with N_2O

$$e_{aq}^{-} + N_2O \rightarrow N_2 + O^{-} \qquad O^{-} + H_2O \rightarrow {}^{\bullet}OH + OH^{-} \quad (2)$$

$$(CH_3)_3COH + OH \rightarrow (CH_3)_2{}^{\bullet}CH_2COH + H_2O \quad (3)$$

produces highly oxidizing conditions upon irradiation and effectively doubles the hydroxyl radical yield. In contrast, adding sufficient concentrations of a hydroxyl radical scavenger, such as *tert*-butyl alcohol (see eq 3), in conjunction with deaerating the solution to remove molecular oxygen, ensures that the predominant reacting radicals are reducing.

Relative rates of TNT transformation in dilute aqueous solution were examined under oxidizing and reducing conditions using γ-radiation. Oxidizing conditions were created by saturating TNT solutions with N_2O prior to irradiation and reducing conditions were induced by adding 1% (v/v) *tert*-butyl alcohol to the stock TNT solution and then sparging with N_2 gas. The results of this comparison are shown in Figure 1. TNT was rapidly transformed under both reducing (*tert*-butyl alcohol, N_2 sparged) and oxidizing (N_2O sparged) conditions. The initial yield for TNT transformation under reducing conditions was 0.14 μmol/J, which was approximately 40% higher than the initial yield of 0.10 μmol/J measured in oxidizing conditions. Thus, these data indicate that, while TNT is labile to both oxidative and reductive transformations, degradation is more efficient under reducing conditions.

Also shown in Figure 1 are data from γ-irradiation of a 220 μmol L^{-1} TNT solution containing 1% *tert*-butyl alcohol that was sparged with O_2 so that the dissolved O_2 concentration was 1.3 mmol L^{-1} prior to irradiation. In these solution conditions *tert*-butyl alcohol served to scavenge the oxidizing radicals while the reducing radicals were expected to react with dissolved O_2 to form reduced oxygen species such as superoxide anion, O_2^-. The yield for TNT transformation during the initial period of the irradiation was 0.013 μmol/J, which was approximately 90% less than was measured in the N_2 sparged solution containing 1% *tert*-butyl alcohol. This result demonstrates that O_2 initially scavenged a majority of the primary reducing radicals. Moreover, this yield suggests that reactions of TNT with the products of oxygen reduction are inefficient in aqueous solution. As a result of reactions with radicals, the dissolved oxygen concentration dropped as the irradiation continued. Consequently, the fraction of reducing radicals reacting with TNT increased, and the TNT decay rate accelerated until, after a dose of approximately 2 kGy, the rate was similar to that measured in the N_2 sparged solution containing 1% *tert*-butyl alcohol. The yield for TNT transformation between 2 and 3 kGy was 0.11 μmol/J.

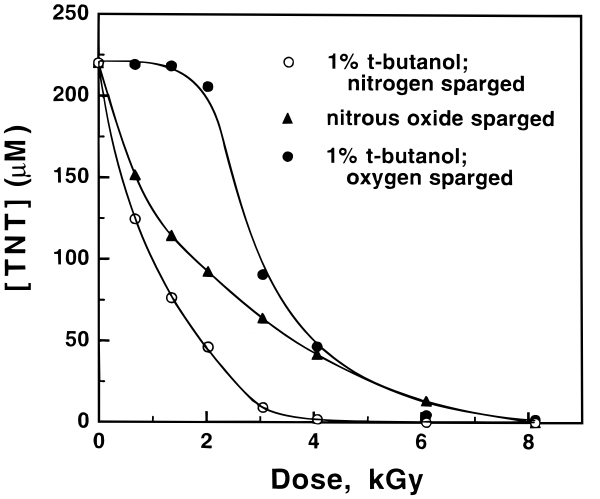

FIGURE 1. Transformation of TNT in aqueous solution induced by γ-radiation under oxidizing and reducing conditions.

No byproducts were identified from the γ-radiolytic transformation of TNT under the reducing conditions described for Figure 1. Compounds which were investigated but not observed include 2-amino-4,6-dinitrotoluene, 4-amino-2,6-dinitrotoluene, and 3,5-dinitroaniline. Under oxidizing conditions 2,4,6-trinitrobenzoic acid (TNBA) was identified as a byproduct. The concentration of TNBA was approximately 16 μmol L^{-1} at a radiation dose of 4 kGy, indicating that oxidation of the methyl group of TNT was an initial transformation step. Oxidation of TNT to trinitrobenzoic acid has been demonstrated by several methods employing strong oxidants (*14, 15*) including aqueous TiO_2 photocatalysis (*7*) where the primary oxidant is the hydroxyl radical (*16*).

In Figure 2 the radiation induced degradation of TNT in oxygen and nitrogen sparged solutions containing no additional radical scavengers is shown. The initial yields for TNT transformation under these conditions were 0.048 and 0.029 μmol/J for O_2 and N_2 saturated solutions, respectively. From data in Figure 1, discussed earlier, it may be assumed that, upon irradiation of the O_2 saturated solution, the primary reducing radicals initially were almost entirely scavenged by O_2 to form reduced oxygen species. This situation is similar to irradiation of the nitrous oxide saturated solution, shown in Figure 1, where the primary reducing radicals were scavenged by N_2O, except that N_2O forms hydroxyl radicals after reacting with e_{aq}^-. Thus, the yield of hydroxyl radicals in the N_2O sparged solution shown in Figure 1 is believed to have been approximately twice that of the O_2 sparged solution in Figure 2. The initial yield for TNT transformation in the O_2 saturated solution (0.048 μmol/J), displayed in Figure 2, was approximately half that measured in the N_2O sparged solution (0.10 μmol/J) in Figure 1. This is further evidence

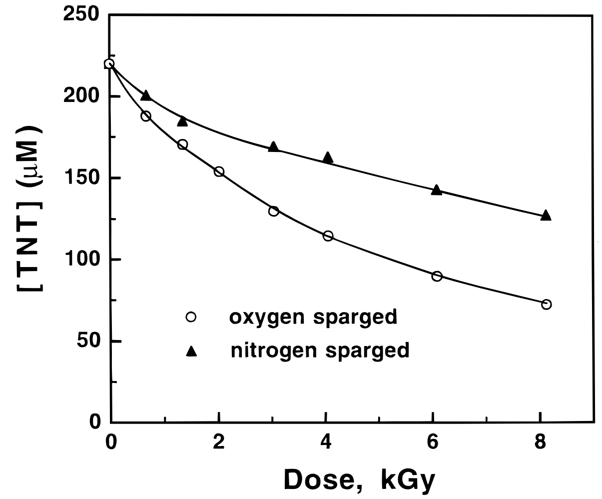

FIGURE 2. γ-Radiation induced transformation of TNT in oxygen and nitrogen sparged solutions containing no additional scavengers.

that TNT is readily degraded by the hydroxyl radical but is relatively unreactive with reduced oxygen species in aqueous solution.

Although TNT is transformed by both e_{aq}^- and $^\bullet$OH, the yield for TNT transformation in the nitrogen sparged solution, as shown in Figure 2, was only 0.029 μmol/J. This low yield suggests that in the absence of a radical scavenger there were significant secondary reactions in which the species resulting from reactions between TNT and the primary radicals further reacted to reform the parent compound. Reactions of this type have been discussed in previous work (*17*). The yield for TNT transformation in the deaerated solution was initially much lower than was observed in the oxygen sparged solution in Figure 2, where O_2 served as an electron and hydrogen atom scavenger. However, as the O_2 concentration decreased at higher radiation doses, the decay rates for the two solutions became essentially the same.

Pulse Radiolysis. Pulse radiolysis was used to determine the rate constants for the reactions of TNT with $^\bullet$OH and e_{aq}^- and to acquire spectral information on the radical species that result from these reactions. As before, solution conditions in which $^\bullet$OH was the predominant radical were created by sparging with N_2O. The absorbance spectrum of the species formed 20−25 μs after the pulse radiolysis of a N_2O saturated 350 μmol L^{-1} solution of TNT is shown in Figure 3. The spectrum displays a broad absorbance in the UV region with a primary maximum at 310 nm and a secondary maximum at 390 nm. The structure of this radical species has not been identified but, based on byproduct analyses from γ-radiolysis discussed above, it is proposed to result predominantly from hydroxyl radical abstraction of a methyl hydrogen to form the trinitrotoluyl radical. The pseudo-first-order rate constant for the formation of this species was measured for five different TNT concentrations in the range 75−350 μmol L^{-1} by monitoring absorbance at 310 nm (see Figure 4). A linear least-squares curve fit of these rate constants vs TNT concentration indicates that the bimolecular rate constant for the reaction between TNT and $^\bullet$OH is 4.3×10^8 mol^{-1} s^{-1}.

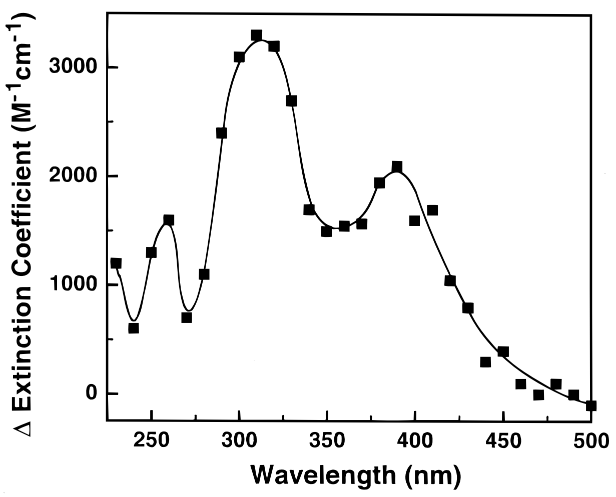

FIGURE 3. Absorbance spectrum of the species formed 20−25 μs after the pulse radiolysis of a N_2O saturated 350 μmol L^{-1} aqueous solution of TNT.

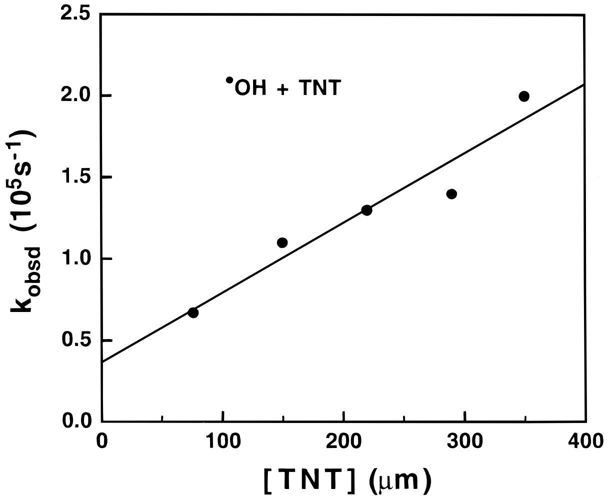

FIGURE 4. Pseudo first-order rate constant as a function of TNT concentration for the reaction between $^\bullet$OH and TNT. Absorbance measured at 310 nm.

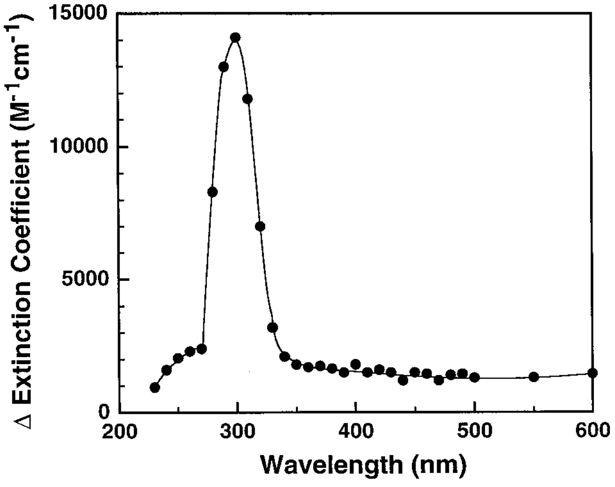

FIGURE 5. Absorbance spectrum of the species formed 100 ns after the pulse radiolysis of a nitrogen sparged 350 μmol L^{-1} aqueous solution of TNT containing 1% *tert*-butyl alcohol.

The reaction between TNT and e_{aq}^- was studied by creating reducing conditions as discussed earlier. The absorbance spectrum of the species formed 100 ns after the pulse radiolysis of a nitrogen sparged 350 μmol L^{-1} TNT solution containing 1% *tert*-butyl alcohol is shown in Figure 5. The spectrum displays a very strong and sharply defined absorbance maximum at 300 nm. On the basis of previous radiolytic studies of other nitroaromatic compounds, this species is proposed to be an electron adduct with the electron localized on one of the electronegative nitro groups (*18*). The pseudo-first-order rate constants for the scavenging of aqueous electrons by TNT were determined at four TNT

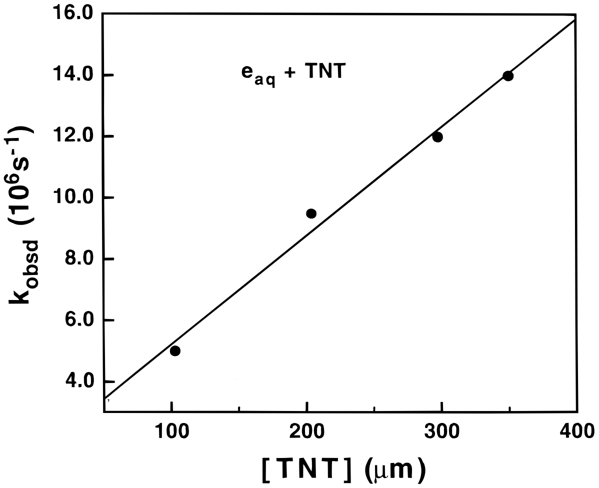

FIGURE 6. Pseudo-first-order rate constant as a function of TNT concentration for the reaction between e_{aq}^- and TNT. Absorbance measured at 300 nm.

concentrations in the range 102−350 μmol L^{-1} by monitoring absorbance at 300 nm (see Figure 6). A linear least-squares curve fit of these rate constants vs TNT concentration indicates that the bimolecular rate constant for the reaction between TNT and e_{aq}^- is 3.5×10^{10} M^{-1} s^{-1}. This value is similar to those reported for the reaction of e_{aq}^- with other nitroaromatic compounds (*19, 20*) and is diffusion controlled. These rate data support the conclusion, noted in the previous section, that TNT will react with both $^{\bullet}OH$ and e_{aq}^- but the rate of reaction with the aqueous electron is significantly higher.

Implications of Radiolysis Studies. The treatment of organic wastes in aqueous systems by currently available advanced oxidation processes relies primarily on the generation of hydroxyl radicals. However, in a previous study of the photocatalytic degradation of TNT in water, using TiO_2 and UV light, we demonstrated that reductive transformations caused by conduction band electrons played a significant role in facilitating the overall degradation of TNT (*12*). This behavior indicated a potential advantage of photocatalysis over other advanced oxidation processes in the treatment of TNT contaminated water. In the present study, we have separately resolved reduction and oxidation of TNT by e_{aq}^- and $^{\bullet}OH$ radicals. TNT was shown to have a significantly higher rate of reaction with e_{aq}^- in comparison to $^{\bullet}OH$, and to degrade more rapidly under reductive conditions. While the reduction potential of e_{aq}^- is greater than that of TiO_2 conduction band electrons, these data clearly suggest that reductive transformation of TNT is a more favorable initial degradation step. In addition, our data demonstrate a relatively low rate of reaction between TNT and reduced oxygen species. Given the low concentrations of TNT typically present in explosives contaminated water and the high rates of reaction between O_2 and reducing radicals, these data show that deaerated conditions are necessary in order to effect reductive degradation of TNT efficiently. Incorporation of these observed kinetics into reactor design, through the utilization of both reductive and oxidative degradation mechanisms, will aid in the development of more efficient methods for treating materials contaminated by nitroaromatic pollutants such as TNT.

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