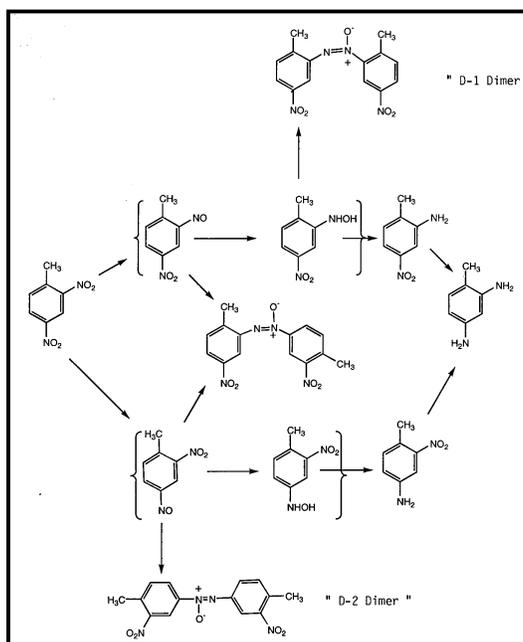# Electrochemical Reduction of Dinitrotoluene

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Devakumaran Meenakshisundaram
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This study evaluated electrochemical reduction of a model nitro aromatic (dinitrotoluene, or DNT) that has shown the tendency to undergo reduction reactions. Objectives were to investigate the effect of stirring rate and the identity of the cathode material on the rate of DNT degradation, and to evaluate the fate of by-products, with specific attention to the mass balance and the potential formation of polymers of the reduced compounds and the parent compound. A bench-scale study was done of the degradation of 2,4-DNT in an electrochemical reactor. The rate of the degradation was measured under various experimental conditions. The by-products of degradation were identified by gas chromatography-mass spectrometry (GC-MS) and GC. A mass balance for the products was obtained under a variety of experimental conditions, both in the aqueous and solid phases. The stirring rate was found to affect the overall rate of degradation in some cases. A satisfactory mass balance for the products was achieved with 2,4-diaminotoluene (DAT) dominating in deoxygenated experiments and the dimers being important in the precipitating solid in the oxygenated experiments.

Foreword

This study was conducted for Headquarters, U.S. Army Corps of Engineers (HQUSACE) under Project 4A161102BT25, "Environmental Research – Corps of Engineers"; Work Unit IB6, "Electrochemical Reduction of Aromatic Compounds."

The work was performed by the Environmental Processes Branch (CN-E) of the Installations Division (CN), U.S. Army Construction Engineering Research Laboratory (CERL). The study was performed in part by the University of Cincinnati, Cincinnati, OH, under contract to the Installations Division. Jennifer L. Jolas and Devakumaran Meenakshisundaram were graduate students associated with the University of Cincinnati. The CERL principal investigator was Stephen W. Maloney. Jerry Benson is Chief, CEERD-CN-E, and Dr. John T. Bandy is Installations Chief, CEERD-CN. The CERL technical editor was William J. Wolfe, Information Technology Laboratory.

The Director of CERL is Dr. Michael J. O'Connor.

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1   Introduction

Background

At many of the U.S. Department of Energy (DOE) and Department of Defense (DOD) sites, an explosives contamination problem has been found in the ground water. There are over 1200 sites with explosives contamination (Tri-service reliance joint engineers 1992). TNT is the most common contaminant found in both the soil and water samples. Other nitroaromatics, especially DNT, have also frequently been found at munitions-contaminated sites (Jenkins and Walsh 1993).

Dinitrotoluene (DNT) has six isomers. The 2,4- and 2,6- isomers are the most important because they are the greatest quantities produced anthropogenically (Beard and Noe 1981). DNT is prepared by the nitration of toluene and nitrotoluene in the presence of nitric and sulfuric acids. DNT is also the major impurity in the production of trinitrotoluene (TNT), due to a partial nitration of the nitrotoluenes. DNT is an important impurity since it comprises nearly 1 percent of the total TNT produced (Ryon et al. 1984). One of the major uses of DNT is as an intermediate in the manufacture of toluene diisocyanate, which is then used in the production of polyurethane foams. Another major use of DNT is as an ingredient in military and commercial explosives; the purified form of 2,4-DNT is used in smokeless powders (Bausum, Mitchell, and Major 1992).

Both TNT and DNT are listed as priority pollutants by the U.S. Environmental Protection Agency (USEPA) because of their toxicological properties. The LD_{50} value in rats for DNT is 268 mg/kg (Sax and Lewis 1989). From a toxicological standpoint, the identification of the products from transformations of nitroaromatic compounds is essential since the resultant products are often more hazardous than the starting compounds.

Objectives

The general goal of this work is to investigate and develop new technologies potentially applicable to the disposal of nitrated explosives. The specific objectives of this study were to provide information regarding: (1) the mechanisms of electrochemical degradation of 2,4-dinitrotoluene (from the point of view of product

studies), and (2) the importance of the nature of the cathode material and the stirring rate in the degradation of 2,4-DNT.

Approach

A bench-scale study was done of the degradation of 2,4-DNT in an electro-chemical reactor, which was fabricated at the beginning of the project. The rate of the degradation was measured under various experimental conditions, which included variations in the stirring rate and the nature of the cathode electrode. The by-products of degradation were identified by gas chromatography-mass spectrometry (GC-MS) and GC. A mass balance for the products was obtained under a variety of experimental conditions, both in the aqueous and solid phases. The degradation behavior was then assessed in light of the experimental results obtained and conclusions are drawn from the data.

Scope

The techniques described in this report apply specifically to Army industrial ac-tivities and were undertaken to benefit the agencies responsible for development and treatment of Army-specific explosives and other aqueous waste streams.

Mode of Technology Transfer

It is anticipated that the results of this basic research will be published as a journal article, and presented at a professional society meeting.

2 Literature Review

Biological Pathways

Two main biological transformations of DNT are oxidation and reduction. Oxidation occurs when oxygen is the reactant and oxygenase or peroxidase enzymes mediate cleavage of the aromatic ring. Reduction is the more common mechanism; it takes place when the nitroaromatic compound is reduced to arylamines by a mechanism of hydrolytic deamination, acetylation, reductive deamination, and cyclization. Until recently, most biological transformations of DNT did not involve total ring cleavage or mineralization.

After studying nearly 200 fungi, Parrish (1977) found that a *Pseudomonas* species degraded both DNT and TNT aerobically with supplemental glucose as a carbon source. Reduction of the nitro groups took place only at the para positions and proceeded through the hydroxylamino-nitrotoluene to the amino-nitrotoluene. McCormick et al. (1978) identified the biotransformation products during the conversion of DNT to 2,4-diaminotoluene (DAT). A fungi *Mucrosporium* aerobically degraded DNT. The identified biotransformation intermediates include: 2-amino-4-nitrotoluene, 4-amino-2-nitrotoluene, 4,4'-dinitro-2,2'-azoxytoluene, 2,2'-dinitro-4,4'-azoxytoluene, and 4-acetamido-2-nitrotoluene. A third azoxy compound, 2,4'-dinitro-2,4'-azoxytoluene or 4,2'-dinitro-4,2'-azoxytoluene, was isolated, but not yet identified conclusively. The hypothetical intermediates of nitroso-nitrotoluene and hydroxylamino-nitrotoluene proposed by McCormick et al. (1978) were successfully identified by Liu et al. (1984). An anaerobic municipal activated sludge system with benzene added as a carbon source showed successful degradation of DNT. For one of the isomers of DNT, 2,6-DNT, degradation under anaerobic incubated sewage conditions was very slow (Hallas and Alexander 1983).

Noguera and Freedman (1996) showed that a *Pseudomonas aeruginosa* strain was capable of reduction and acetylation of DNT. Under anoxic conditions, the main products were 2-amino-4-nitrotoluene and 4-acetamide-2-nitrotoluene. Also, 4-amino-2-nitrotoluene was very rapidly acetylated to 4-acetamide-2-nitrotoluene, and 2-amino-4-nitrotoluene was very slowly degraded to DAT and 2-acetamide-4-nitrotoluene. Formation of DAT from 4-amino-2-nitrotoluene by *Pseudomonas aeruginosa* has a very low yield. The biotransformation of DNT

was carried out with denitrifying cultures, which were acclimated to the treatment of munitions wastewater (Noguera and Freeman 1997). The main extractable intermediates and products were 2-aminotoluene, 4-nitrotoluene, 4-acetamide-2-nitrotoluene, 4-acetamidetoluene, and 6-nitroindazole. For most of these compounds, this was the first report of their presence as intermediates and products in a biological treatment system.

Spanggord et al. (1991) showed the ability to completely mineralize DNT by an oxidative pathway with a *Pseudomonas* species using DNT as the sole carbon source. The nitro groups were removed without reduction to amines. Dioxygenase attack was responsible for the nitro group reduction and a subsequent release as nitrite. Valli et al. (1992) were able to degrade DNT by the lignin-degrading fungus *Phanerochaete chrysosporium*. This fungus contained two peroxidases, which are responsible for the complete mineralization of DNT to CO_2 in nitrogen-limiting cultures. The treatment of DNT using a two-stage system has also been shown to completely mineralize DNT with 2-amino-4-nitrotoluene and 4-amino-2-nitrotoluene as intermediates (Berchtold et al. 1995).

Hydrogenation with Metal Catalysis

Palladium, platinum, and Raney nickel are common catalysts for the hydrogenation of nitrosubstituted aromatic compounds. Raney nickel catalysts, when heated from room temperature to about 400 °C, evolve 50 to 200 mL of hydrogen per gram of nickel. Raney nickel can also act as a reducing agent by furnishing its own supply of hydrogen, from within its lattice, without being heated (Yao and Emmet 1962). In the Raney nickel hydrogenation of nitrobenzene, the intermediates (azoxybenzene and azobenzene) were isolated by Burge et al. (1980). These observed intermediates verified that the Haber process also occurs in the hydrogenation reaction from nitrobenzene to aniline with Raney nickel.

Palladium-catalyzed hydrogenation has been found to completely reduce DNT to DAT (Janssen et al. 1980). Palladium on carbon was used as the catalyst for these studies. Terpko and Heck (1980) were able to selectively reduce one nitro group of the dinitroaromatic compound with a palladium catalyst. For DNT, the less hindered or para position was reduced with a very high yield (92 percent). However, for the four other 2,4-dinitroaromatic compounds tested (with -OH, -OCH_3, -NH_2 and -$NHCOCH_3$ groups instead of - CH_3), the more hindered or ortho position was reduced. Janssen et al. (1990) found two parallel reaction pathways for the formation of DAT from DNT in a palladium catalyzed hydrogenation reaction. There were three stable reaction intermediates: 4-hydroxylamino-2-nitrotoluene, 4-amino-2-nitrotoluene, and 2-amino-4-nitrotoluene. Very low con-

centrations of 4-hydroxylamino-2-nitrotoluene were found. This suggested that the nitro group in the ortho position was converted almost directly to the amino group.

Nitroaromatic compounds undergo reductive transformations to aromatic amines. The reduction of nitroaromatics occurred through a series of electron-transfer reactions and protonations with nitroso compounds and hydroxylamines as highly reactive intermediates. Barrows et al. (1996) found that the location of the first nitro group reduced was influenced by the regioselectivity for substituted polynitroaromatic compounds. The regioselectivity was important in the first proton transfer to the radical anion that was created after the initial one electron reduction of the starting compound. Localization of the charge in the initial radical anion influenced the site of protonation. Of the 10 polynitroaromatic compounds studied, all except two showed localization of the radical ion on the nitro group in the ortho position. The two with the localized radical ion in the para- position were DNT and TNT. DNT showed an 88 to 92 percent regioselectivity for the para- position and TNT showed a 100 percent regioselectivity.

Electrochemical Pathways

The nitrogen in the nitro group is already at a high oxidation state, +3. There is no known anodic chemistry of DNT since it is extremely difficult to remove an electron (Fry 1982). Many studies have been carried out on the electrochemistry of nitro-organics. The nitrosobenzene intermediate was rarely observed (Shindo and Nishihara 1989; Martigny and Simmot 1983), although evidence for its formation has been observed by the formation of the azoxy and azobenzene dimers (Laviron and Vallat 1973). For the reduction of nitroaromatic compounds by zero-valent Fe under anaerobic conditions, no azo or azoxy dimers were found with the Fe^0 reduction.

Electrochemical reduction of nitrated organic compounds has been studied in nonaqueous solvents from the viewpoint of methods for synthesis of organic chemicals.   Evans and coworkers have studied the reduction of 1,1-dinitrocyclohexane (Bower and Evans 1988; Ruhl et al. 1991) and several nitro-alkanes (Ruhl et al. 1992) in dimethylformamide. They demonstrated that these protective nitro groups could be reduced by electrochemistry. In a related study (Kopilov and Evans 1990), it was found that dehalogenation can occur when electrochemical reduction is applied to a-haloacetanilides in alcohol and acetonitrile. These same groups (nitro- and halo-) protect the compounds from biological attack. These studies in organic solvents suggest that the conversion may also be

possible by the use of electrodes in water, for the purpose of opening up the contaminant to conventional biodegradation.

3   Electrochemical Degradation of 2,4-DNT

Important Parameters

The role of stirring rate and electrode material was also examined. The product identity is an important consideration for any degradation process development, so the identification of the products was one additional major focus of the study.

Experimental Setup

The reactor used in this experiment is a clear glass reactor with a liquid volume of 2200 mL. The anode is a platinum wire. (Platinum was chosen for its resistance to corrosion.) There are several options for the use as the cathode (some of which have been previously investigated and reported in a study sponsored by CERL). One option is a high density fine grain graphite cylinder with an outer diameter of 83 mm, an inner diameter of 63 mm, and a length of 152 mm[*] (Table 1). Another option is a glassy carbon rod (zero porosity, see Table 2) with a diameter of 7 mm and a length of 150 mm. A third option is a titanium mesh wire cylinder, which provides more surface area. The dimensions of the titanium cathode made of a titanium wire cloth are an outside diameter of 77 mm with a thickness of 1 mm and a length of 150 mm. The salt bridge used in the experiments is filled with a slurry of Na_2SO_4. The anode can be placed at the end of the salt bridge. Figure 1 shows a diagram of the reactor.

For all experiments, 18 MW-cm resistivity water was used (distilled and deionized). A 0.02 M phosphate buffer (pH = 8) was used to maintain pH. The salt concentration was usually kept constant at about 36 g/L of Na_2SO_4 (Fisher Scientific, Pittsburgh, PA). 2,4-Dinitrotoluene from Aldrich Chemical, Milwaukee, WI, was used as received. The 2,4-DNT was used to make up a stock solution of 1.22 g 2,4-DNT in 20 g of acetone. A specific volume of this 48.3 g/L stock solution

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[*] From Graphite Sales, Inc., Chagrin Falls, OH.

was pipetted into the reactor for each experiment. The experiments were carried out with continuous stirring by a magnetic stir bar resulting in rotations of the bar from 540 to 2500 rpm. The external power supply maintained a steady current allowing the voltage to fluctuate.

Table 1. Physical properties of high density fine grain graphite.

Property	Metric Units
Maximum grain size	0.84 mm
Apparent density	1.68 g/cm^3 - 1.71 g/cm^3
Total porosity	21 %
Electrical resistivity	65 - 75 micro ohm - cm x 10^{-5}
Flexural strength	170 - 240 kg/cm^2
Compressive strength	300 - 400 kg/cm^2
Tensile strength	110 - 155 kg/cm^2
Modules of elasticity	1100 - 1250 kg/mm^2
Ash	0.20 %

Table 2. Physical properties of the glassy carbon cathode.

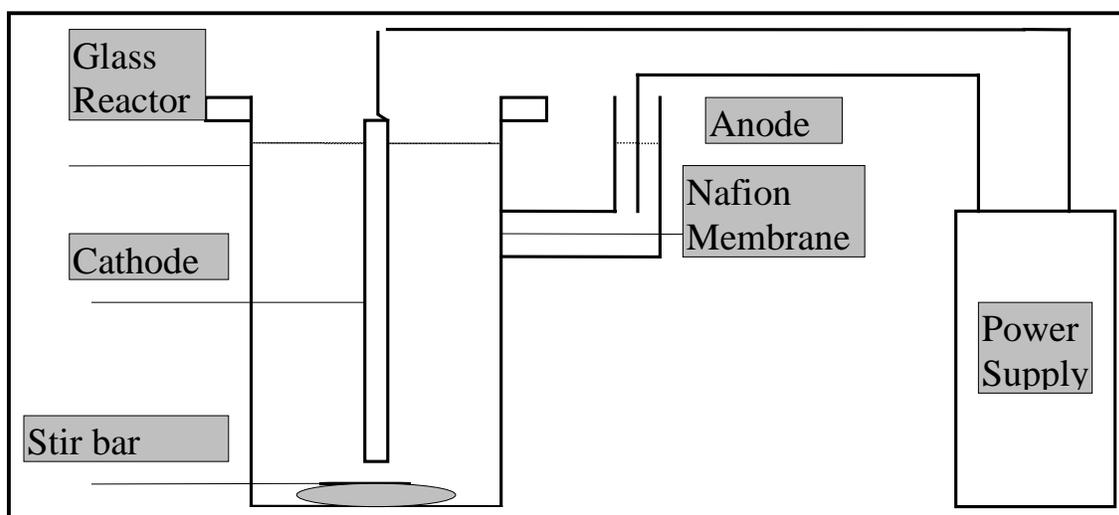| Property	Metric Units
Maximum grain size	—
apparent density	1.42 g/cm^3
Total porosity	0 %
Electrical resistivity	4.4 x 10^3 µ ohm-cm
Flexural strength	2.6 x 10^5 kg/ cm^2
Compressive strength	4.8 x 10^5 kg/ cm^2
Tensile strength	—
Modules of elasticity	35000 kg/ mm^2
Ash	0 %

Figure 1. Experimental setup.

Analytical Techniques

The length of time for one experiment was always less than 12 hours. Six to eight samples were taken at regular intervals in each experiment. When the samples were taken, pH, voltage, dissolved oxygen (DO), oxidation reduction potential (ORP), and conductivity were also monitored. Samples for the GC were withdrawn from the reactor with a 2.5 mL pipette. The samples were then extracted into 0.5 mL of dichloromethane with vigorous shaking for 2 minutes. An internal standard of quinoline was used for analysis precision. Samples for GC-MS for product identification were withdrawn from the reactor once or twice; a larger 50 mL sample was taken and extracted into benzene, dichloromethane, or diethyl ether. At the end of each experiment, 250 mL was saved for further extraction to examine final products. All samples were kept at 4 °C until analyzed.

The GC analysis allowed the monitoring of the degradation of DNT and the formation of intermediates and products. The GC instrument used in the analysis is an HP 5890 Series II with an FID detector, with a 30 m x 0.32 mm inside diameter (i.d.) fused silica capillary column and 0.25 mm film thickness (J & W Scientific, DB-1), and a carrier gas of nitrogen (80 psi). The GC-MS analysis allowed the identification of stable intermediates and final products. The GC-MS instrument is an HP 5890 GC and MS 5970, a selective mass ion detector, 30 m x 0.25 mm i.d. fused silica capillary column and 0.25 mm film thickness (J & W Scientific, DB-5), and a carrier gas of He (50 psi).

The ORP was measured using a double-junction ORP electrode (Cole Parmer Instrument Co., Vernon Hills, IL) with a platinum band. The electrode was tested before use with two different buffers (pH 4.0 and 7.0), which were saturated with Quinhydrone (Aldrich Chemical Co., Milwaukee, WI). This test showed that the calibration was correct and that the probe was functioning properly according to the range of ORP values given by the manufacturer. The ORP electrode was rinsed with deionized water and the ORP was measured directly in the reactor.

Synthesis of Selected Degradation Products

Due to the commercial unavailability of some of the expected products, a literature search was conducted to assess the feasibility of synthesizing them in the laboratory. The following experimental methods were employed for the synthesis of selected by-products.

Synthesis of 4,4'-dinitro-2,2'-azoxytoluene (McCormick et al. 1978)

1. 1.52 g (10 mmol) of 2-amino-4-nitrotoluene (Aldrich Chem. Co.) was added to 75 ml of dichloromethane.
2. 4.1 g (20 mmol) of m-chloroperoxybenzoic acid (Aldrich Chem. Co.) was added to the above solution and allowed to stand overnight.
3. The precipitate of chlorobenzoic acid was removed by filtration and the filtrate extracted with 5 percent aqueous sodium bicarbonate solution.
4. The dichloromethane was allowed to evaporate and the resulting precipitate was recrystallized with 95 percent ethanol.
5. A slightly yellow solid of the dimer was collected.
6. The above procedure is repeated with 4-amino-2-nitrotoluene as the starting compound to produce the other isomer.

Synthesis of Caro's Acid

1. 145 g (0.64 moles) of ammonium persulfate was added to 54 ml of cold, concentrated H_2SO_4.
2. The mixture was allowed to stand for about an hour and poured into 355 g of crushed ice.

Synthesis of 2-nitro,4-nitroso Toluene

1. A cold suspension of 3.5 g (0.23 mole) of 2-nitro,4-amino toluene in 6 ml of sulfuric acid and 1 ml of water is mixed in an ice bath for 1 hour.
2. Caro's acid is added to the above and stirred for 17 hours. The yellow precipitate was recrystallized with acetone.

Degradation Behavior as a Function of Stir Rate and Electrode Material

Experiments with varying currents showed that the optimum 2,4-DNT conversion can be achieved at currents of about 50-70 mA. The effect of stirring was not as great as expected. Results for the titanium mesh wire indicate very little difference between 540 and 2500 rpm (Table 3). For the graphite cylinder cathode (Tables 4 and 6), the effect of stirring on the rate of 2,4-DNT degradation was only significant at 53 and 65 mA. For the glassy carbon cathode (Tables 5 and 7), the effect of stirring on 2,4-DNT degradation was very small. It is believed that the hydrogen film (which will form on the cathode surface) impedes the rate of the electrochemical degradation of 2,4-DNT only in cases where porosity of the cathode is significant (see Table 1) as is the case for the graphite cylinder. Glassy carbon (Table 2), on the other hand, has zero porosity and thus the hydrogen film attachment is much weaker. For the titanium mesh wire, the porosity is also expected to be very low (not measured). The effect of the surface area of the cathode was investigated. In Table 8, the rate of degradation with a glassy

carbon cathode is tabulated with the available surface area. It is clear that a linear relationship exists between the available surface area and the rate of degradation of 2,4-DNT (Figure 2).

Table 3. Experimental data for titanium wire mesh cylinder.

Current (mA)	Stir Rate (rpm)	Dissolved Oxygen	Rate Constant (min^{-1})
23	540	Oxygenated	0.0036
23	2500	Oxygenated	0.0029
39	2500	Oxygenated	0.0071
39	540	Oxygenated	0.0069
39	2500	Deoxygenated	0.017
39	2500	Deoxygenated	0.015
39	540	Deoxygenated	0.016
45	540	Oxygenated	0.014
45	2500	Oxygenated	0.014
45	2500	Deoxygenated	0.022
53	540	Oxygenated	0.020
53	2500	Oxygenated	0.018
53	2500	Deoxygenated	0.028
65	540	Oxygenated	0.023
65	2500	Oxygenated	0.025
65	540	Deoxygenated	0.034
65	2500	Deoxygenated	0.035
65	2500	Deoxygenated	0.037
72	2500	Oxygenated	0.028
72	540	Oxygenated	0.027
72	2500	Deoxygenated	0.056

* Initial DNT at 46.4 mg/L and [Na$_2$SO$_4$] at 36.4 g/L.

Table 4. Experimental data for graphite cylinder (oxygenated), surface area is 722 cm^2.

Current (mA)	Stir rate (rpm)	Rate Constant (min^{-1})	Rate Constant (min^{-1} cm^{-2}) (x 10^5)	Molar % Converted to DAT*	
23	540	0.0045	0.623	9.7	(3.68)
23	2500	0.0009	0.125	0.0	(0.00)
45	540	0.007	0.97	23.0	(7.72)
45	2500	0.0088	1.22	22.0	(5.30)
53	540	0.0106	1.5	47.4	(15.90)
53	2500	0.0154	2.13	44.7	(15.07)
65	540	0.0076	1.05	15.3	(5.13)
65	2500	0.01	1.39	12.5	(4.19)

* The value in the parenthesis is the concentration of DAT in ppm.

Table 5. Experimental data for glassy carbon (oxygenated), surface area is 57.9 cm^2.

Current (mA)	Stir Rate (rpm)	Rate Constant (min^{-1})	Rate Constant (min^{-1} cm^{-2}) (x 10^5)	Molar % Converted to DAT*	
23	540	0.0039	5.78	0.0	(0.0)
23	2500	0.0044	6.52	0.0	(0.0)
45	540	0.0048	7.11	22.2	(5.8)
45	2500	0.0062	9.19	7.6	(2.14)
65	540	0.005	7.40	45.45	(13.1)
65	2500	0.0068	10.0	23.2	(6.74)
* The value in the parenthesis is the concentration of DAT in ppm.					

Table 6. Experimental data for graphite cylinder (deoxygenated), surface area is 722 cm^2.

Current (mA)	Stir Rate (rpm)	Rate Constant (min^{-1})	Rate Constant (min^{-1} cm^{-2}) (x 10^5)	Molar % Converted to DAT*	
23	540	0.005	0.69	22.3	(6.53)
23	2500	0.0059	0.82	23.3	(6.37)
45	540	0.0125	1.73	51.56	(18.04)
45	2500	0.0139	1.93	33.26	(10.52)
53	540	0.0145	2.00	25.63	(9.04)
53	2500	0.0144	2.00	19.96	(7.78)
65	540	0.0105	1.45	45.0	(15.07)
65	2500	0.0168	2.33	20.25	(6.41)
* The value in the parenthesis is the concentration of DAT in ppm.					

Table 7. Experimental data for glassy carbon (deoxygenated), surface area is 57.9 cm^2.

Current (mA)	Stir Rate (rpm)	Rate Constant (min^{-1})	Rate Constant (min^{-1} cm^{-2}) (x 10^5)	Molar % Converted to DAT*	
23	540	0.0042	6.22	76.7	(25.7)
23	2500	0.0047	6.96	96.0	(32.0)
45	540	0.0040	5.93	98.0	(28.2)
45	2500	0.0048	7.11	95.0	(27.7)
65	540	0.0053	7.85	70.0	(20.9)
65	2500	0.005	7.4	78.9	(24.4)
* The value in the parenthesis is the concentration of DAT in ppm.					

Table 8. The effect of surface area of cathode on the reaction kinetics with the glassy carbon cathode, current at 65 mA, stir rate at 2500 rpm.

Surface Area (cm^2)	Rate Constant (min^{-1})
67.13	0.0080
57.90	0.0077
44.75	0.0049
31.33	0.0035

The chart shows Rate Const (1/min) on the y-axis versus Surface Area (cm2) on the x-axis.

Chart annotations:
$$y = 0.0001x - 0.0009$$
$$R^2 = 0.9547$$

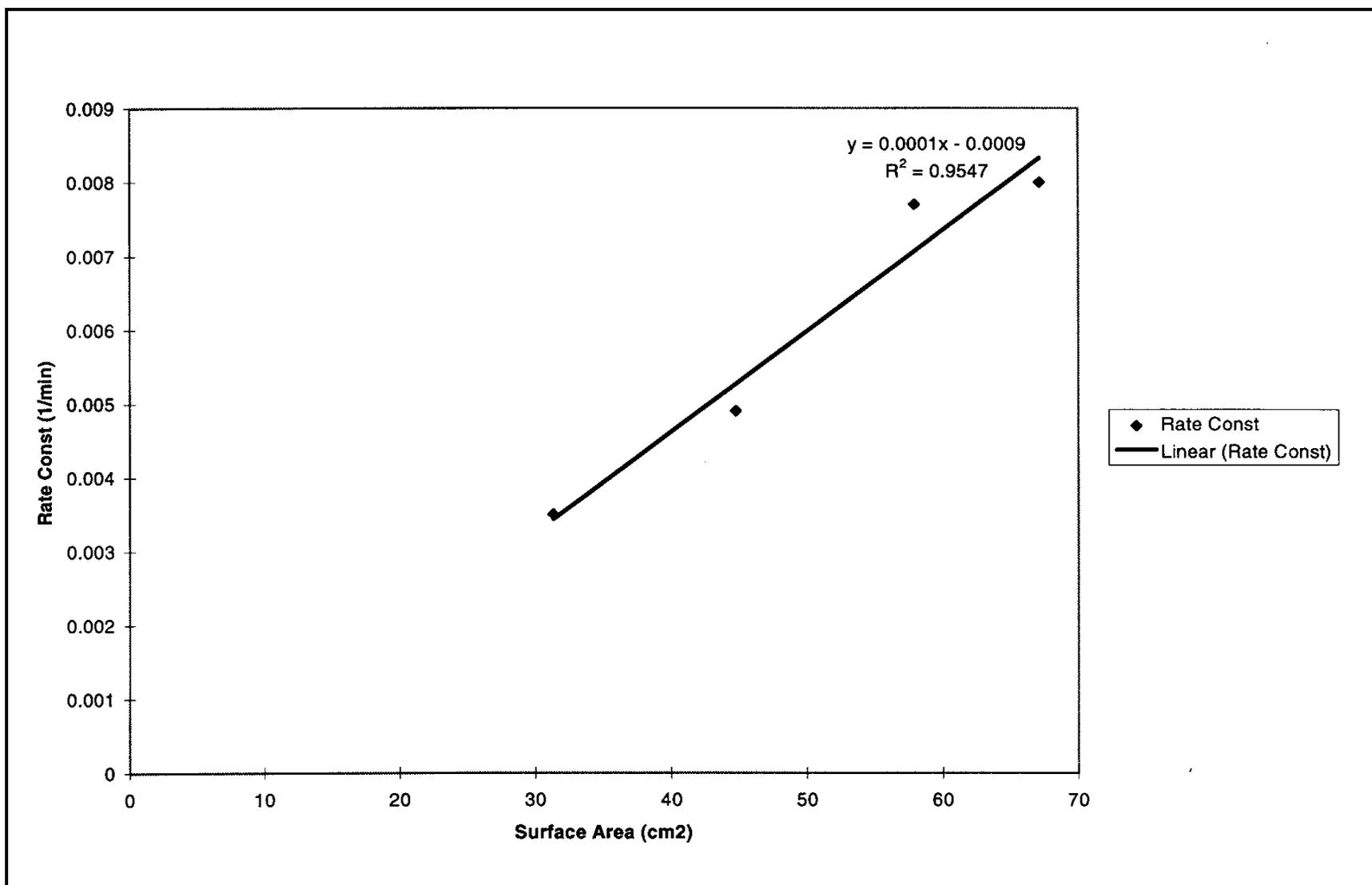Legend:
◆ Rate Const
— Linear (Rate Const)

Figure 2. Effect of surface area of the electrode on the rate of DNT degradation.

Product Studies and Mass Balance

Intermediates and end-products have been identified in most experiments. A good mass balance was achieved for experiments with varying currents, oxygen conditions, and varying cathode materials (Tables 9 to 13). The percentage yields on a molar basis vary from 70 to 115 percent. Any value above 100 percent is obviously due to experimental error. Therefore, an error of about 15 percent can be used for the interpretation of the results. A second important finding from this study is that a large fraction of the products in many experiments is present in the solid precipitate that is formed during the degradation of 2,4-DNT and that remains suspended in the reactor. For instance, in the case of glassy carbon at 2500 rpm in oxygenated solution at 45 mA, more than 70 percent of the products on a molar basis is in the solid phase (Table 10). The solid phase consists primarily of the D-2 (i.e., 2,2'-dinitro,4,4'-azoxytoluene) dimer, with a minor contribution from the D-1 (i.e., 4,4'-dinitro,2,2'-azoxytoluene) dimer. In contrast, the diaminotoluene (i.e., DAT) and 2-nitroso,4-nitrotoluene are found in the aqueous phase. It is known that some of the degradation products, such as the two dimers mentioned above, are much less soluble in water compared to 2,4-DNT and thus they precipitate out of the water once their concentration increases and supersaturation occurs. One can use the data listed in Tables 9 to 13 to compare the amount of each identified product both in the aqueous phase and in the solid phase. Note that especially the dimers partition into the solid phase very readily and effectively, while the DAT, the nitroso compound, and the amino-nitrotoluene remain primarily in the aqueous phase. Figures 3 to 7 show the time profiles of the products. Note that many of the observed products were only observed as intermediates and not as stable final products. When the reaction medium was sampled at the end of the experiment, very little of the amino-nitrotoluene was found. Furthermore, the aqueous phase concentration of the dimer always decreases as a function of time as the solid starts to form and begins to remove the dimers from the aqueous phase (Figures 3 to 7).

Based on the product studies and the mass balance shown in Figures 3 to 7 and in Tables 9 to 13, one can assess the importance of the relative pathways in the mechanistic scheme of 2,4-DNT degradation shown in Figure 8. Based on the products identified, the pathways that dominate in deoxygenated experiments involve the direct transformation of 2,4-DNT to 2,4-DAT via the nitroso and hydroxylamine intermediates (neither of which have actually been experimentally observed). No other products or intermediates have been isolated in deoxygenated experiments.

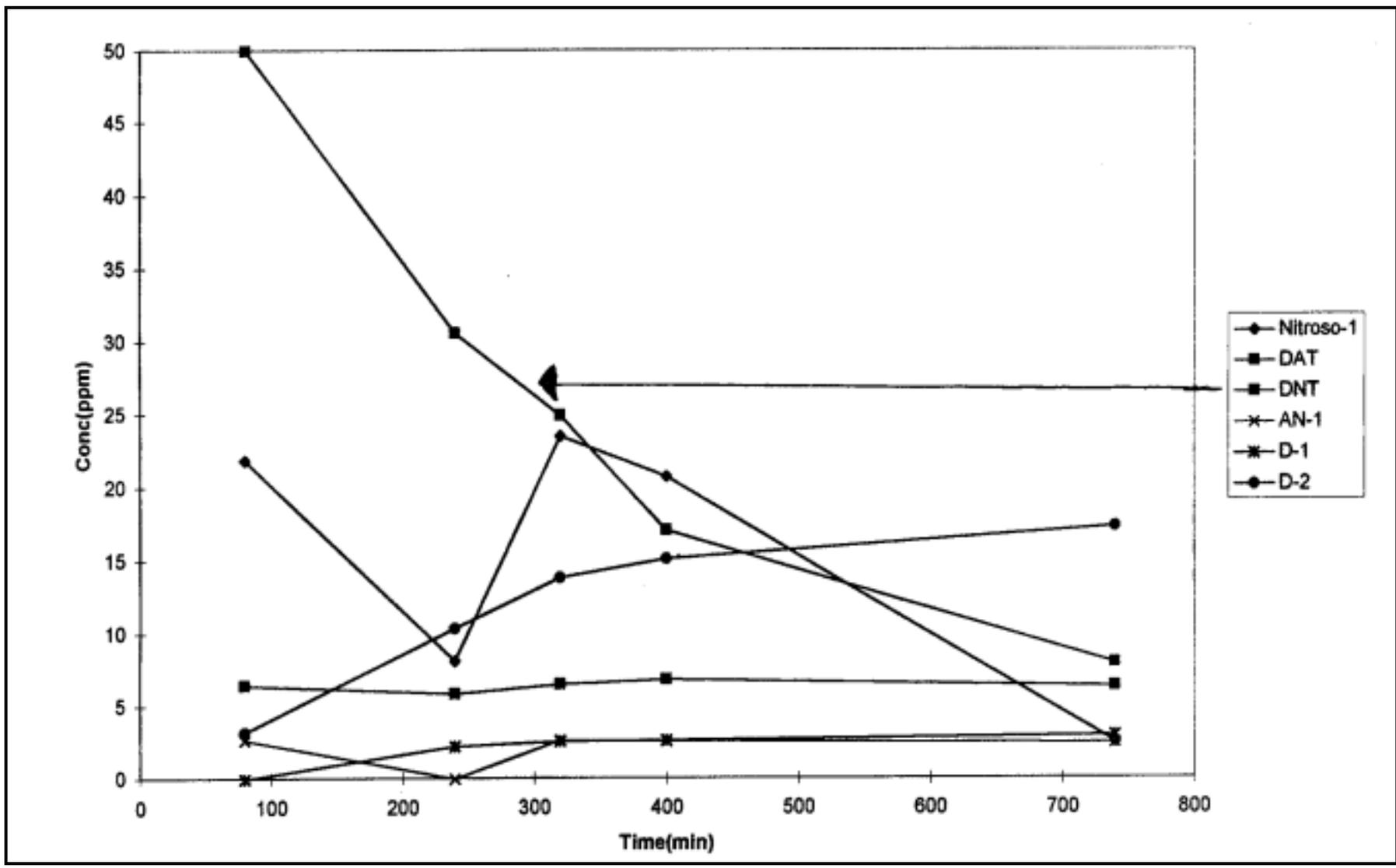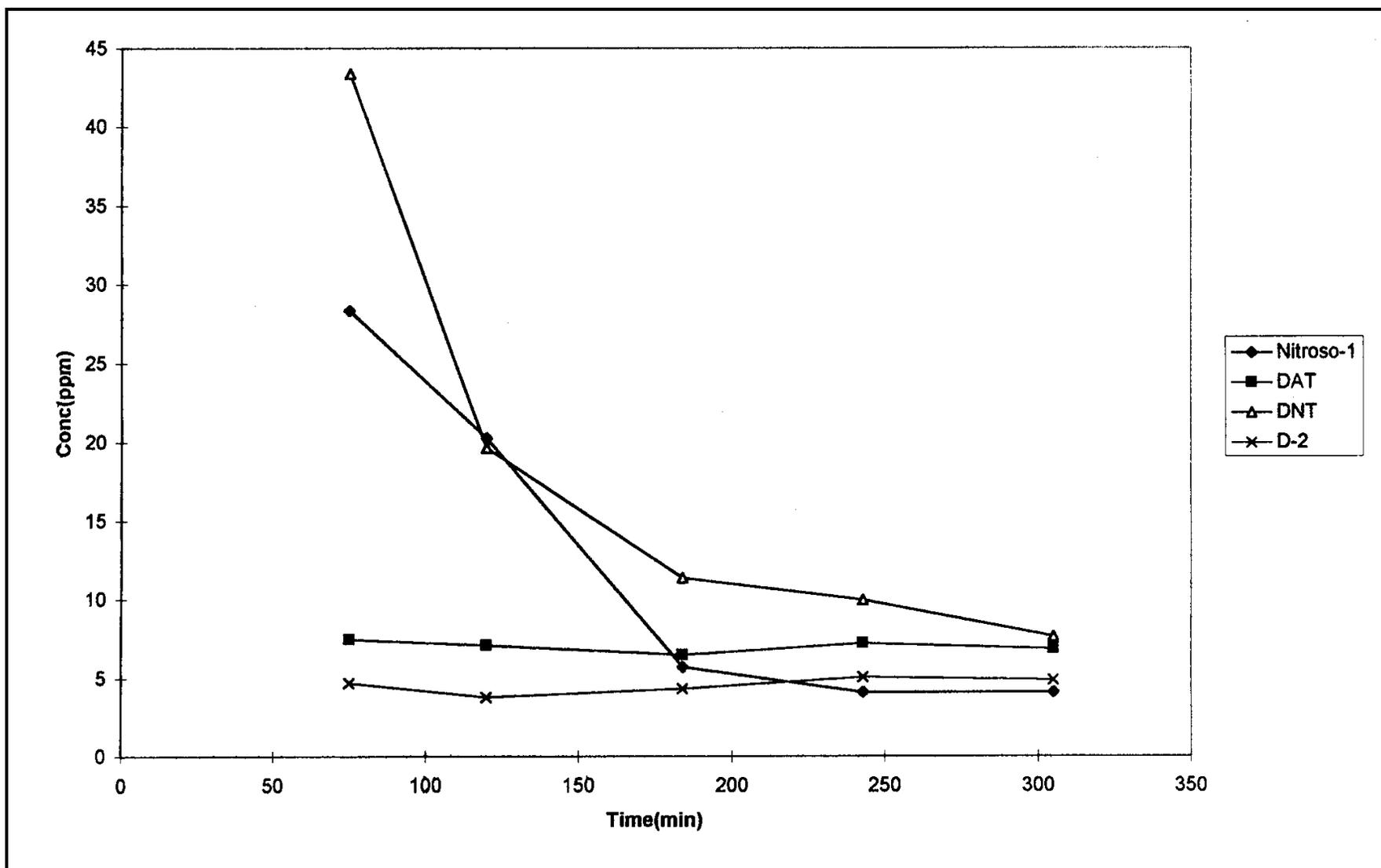**Figure 3. Product evolution for a glassy carbon (23 mA, open).**

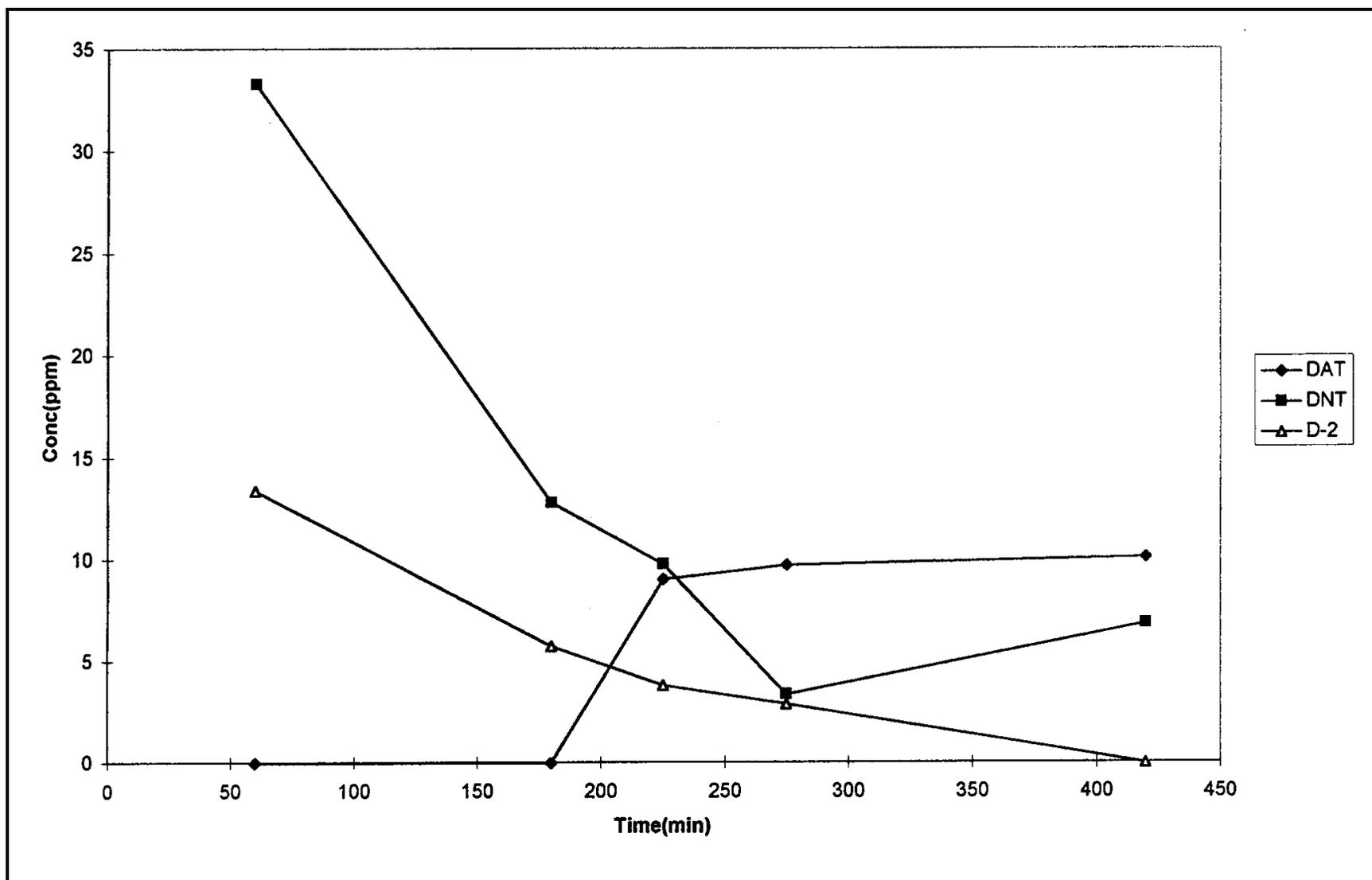Figure 4. Product evolution for a glassy carbon (45 mA, open).

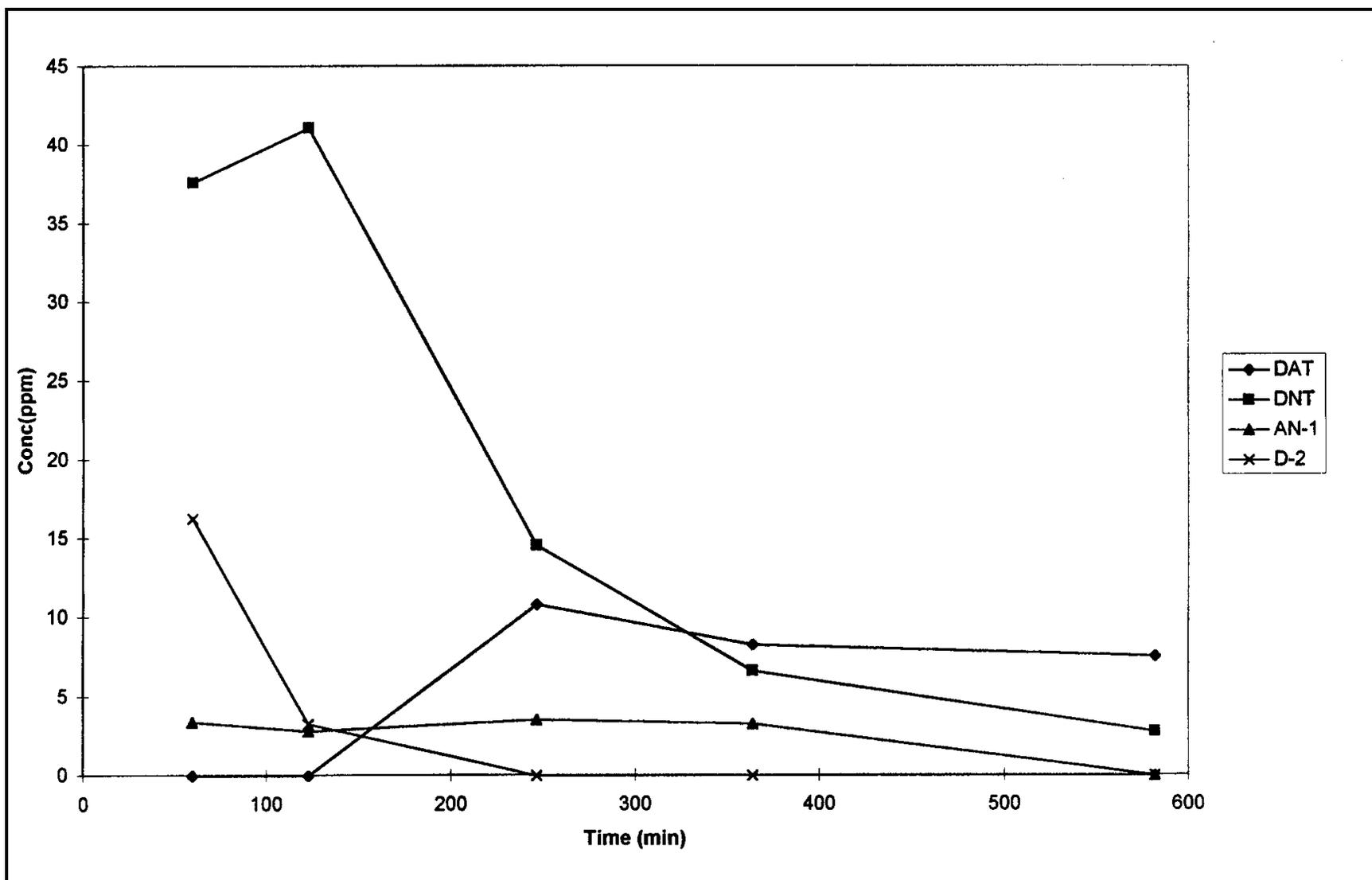**Figure 5. Product evolution for a glassy carbon (65 mA, open).**

Figure 6. Product evolution for a graphite cylinder (45 mA, open).
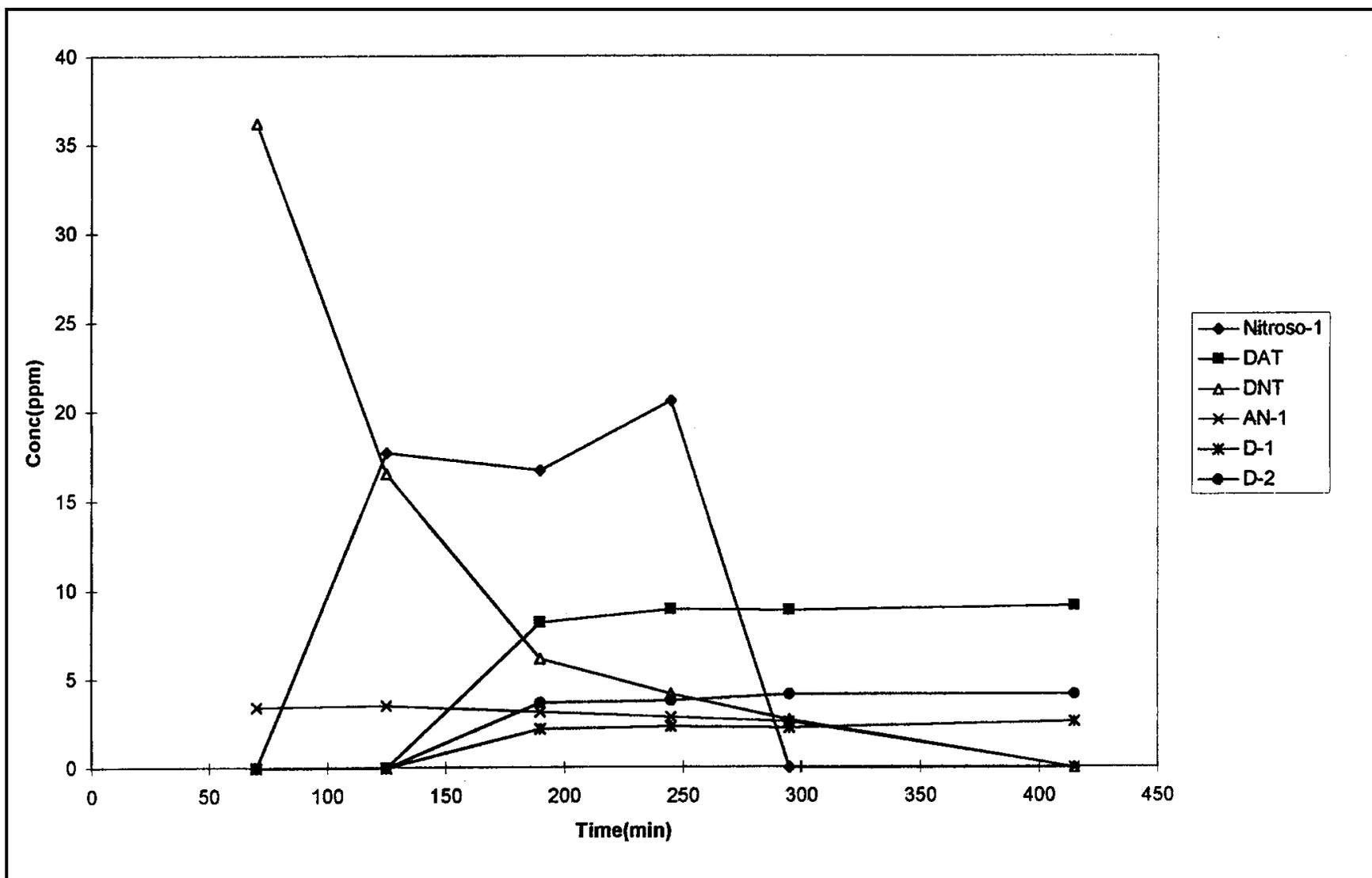
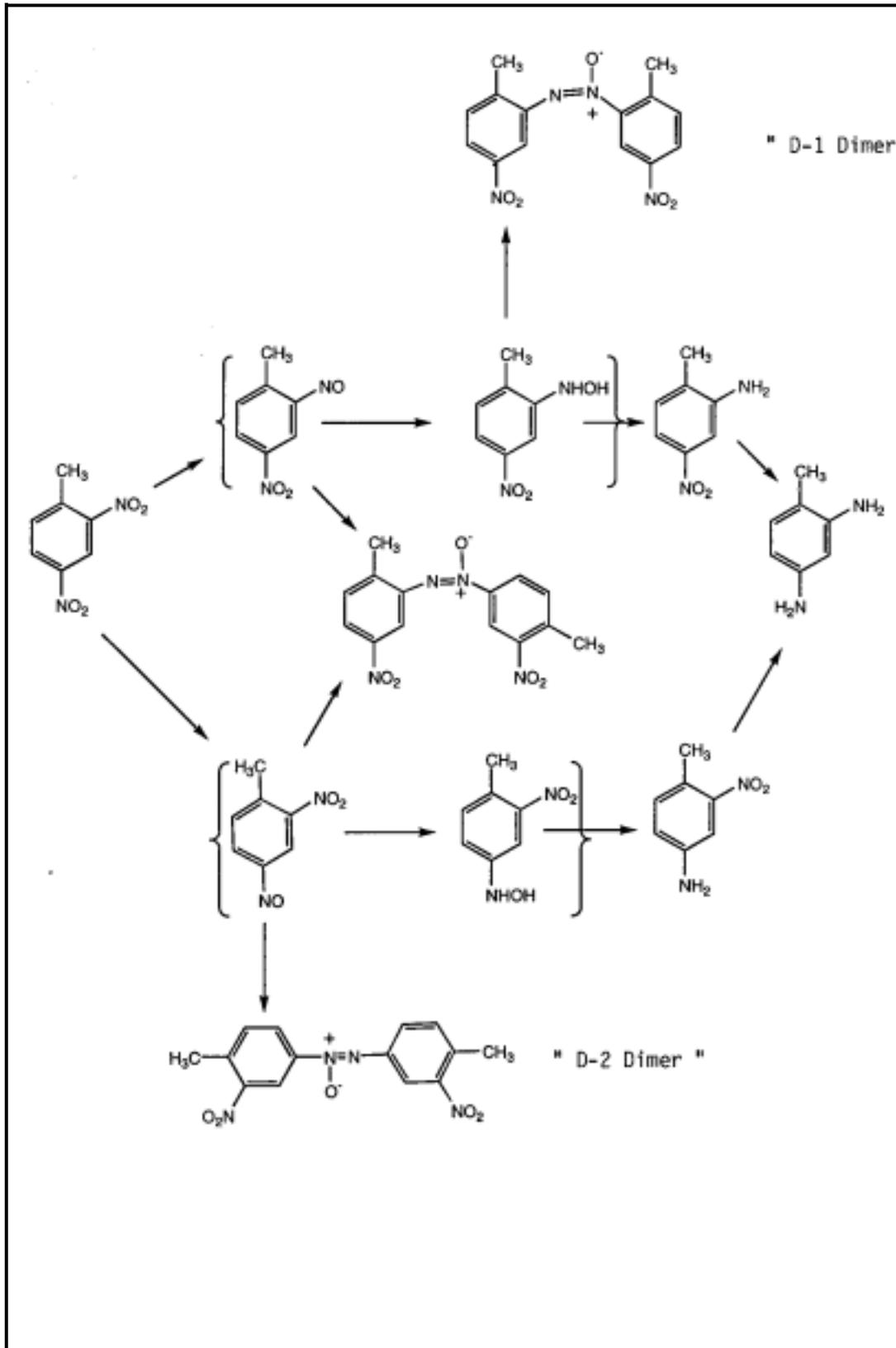Figure 7. Product evolution for a graphite cylinder (65 mA, open).

Figure 8. Overall mechanistic scheme of 2,4-DNT degradation (McCormick et al. 1978).

In the oxygenated experiments, the situation is much more complicated, with dimers, the amino-nitrotoluenes, and the nitroso compounds being present at different times of the degradation process (Figures 3 to 7). For instance, the degradation of 2,4-DNT at 23 mA with a glassy carbon (Figure 3), the profile of the 2-nitroso,4-nitrotoluene (Nitroso-1) is very dynamic. Its concentration reaches the maximum at around 300 minutes, but drops off toward the end of the degradation to a value of less than 5 ppm.

The concentration of the most dominant dimer, D-2, starts low and increases smoothly to a level of about 15 ppm and remains at this level until the end of the experiment. It is important to remember that the profiles shown in Figure 3 only depict the aqueous concentrations. The solid phase concentrations are not shown in the figure. The two dimers found in the degradation of 2,4-DNT, which are almost always found in the suspended solid precipitate, are shown in the top and bottom parts of Figure 8. There is no evidence for the presence of the mixed (i.e., non-symmetrical) isomer depicted in the middle of the mechanistic scheme (Figure 8). It is noteworthy that the formation of the solid phase also influences the aqueous phase concentrations of some of the compounds significantly (see Table 10 for an example). The data in Table 10 show that a large fraction of the total products produced is found in the solid precipitate and that the aqueous concentrations only account for about one third of the total mass balance. Therefore, it is very important to sample and analyze both the aqueous phase and any solids formed during electrochemical degradation of 2,4-DNT under oxygenated conditions.

Table 9. Mass balance with the graphite cylinder cathode, at 2500 rpm, oxygenated.

Current (mA)	Compounds*	Solid Phase (% Molar Conversion of DNT to)	Aqueous Phase (% Molar Conversion of DNT to)
65	DAT	—	28.5
65	D-1	2.23	4.21
65	D-2	43.9	—
65	Total	46.13	32.71
Total Mass Balance (% Molar Conversion of DNT to identified products) = 78.8 %			
45	DAT	—	23
45	D-2	87.8	—
45	Total	87.8	23
Total Mass Balance (% Molar Conversion of DNT to identified products) = 110 %			

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* *Product abbreviations used in tables 9-12:* Nitroso-1= 2-nitroso,4-nitrotoluene; AN-1 = 2-amino,4-nitrotoluene; AN-2 = 4-amino,2-nitrotoluene; DAT = 2,4-diaminotoluene; D-1 = 4,4'-dinitro,2,2'-azoxytoluene; D-2 = 2,2'-dinitro,4,4'-azoxytoluene.

Table 10. Mass balance with the glassy carbon cathode, at 2500 rpm, oxygenated.

Current (mA)	Compounds	Solid Phase (% Molar Conversion of DNT to)	Aqueous Phase (% Molar Conversion of DNT to)
65	DAT	—	37.7
65	D-2	58.7	—
65	Total	58.7	37.7
Total Mass Balance (% Molar Conversion of DNT to identified products) = 96.4 %			
45	DAT	—	24.2
45	Nitroso-1	—	10.7
45	D-1	7.7	—
45	D-2	65.96	—
45	Total	73.66	34.9
Total Mass Balance (% Molar conversion of DNT to identified products) = 109 %			
23	DAT	—	22.7
23	Nitroso-1	—	6.6
23	AN-1	—	7.13
23	D-1	7.89	—
23	D-2	42.9	27.6
23	Total	50.8	64
Total Mass Balance (% Molar conversion of DNT to identified products) = 115 %			

Table 11. Mass balance with the glassy carbon cathode, deoxygenated.

Current (mA)	Stir Rate (rpm)	Dissolved Oxygen	DAT Conc. in ppm (% Molar Conversion of DNT to DAT)
23	540	0.2	25.7 (76.7)
23	2500	0.2	32.0 (96.0)
45	540	0.2	28.2 (98.0)
45	2500	0.2	27.7 (95.0)
65	540	0.2	20.9 (70.0)
65	2500	0.2	24.4 (78.9)

Hydrogen Gas Experiments

Two sets of hydrogen gas experiments were conducted to determine whether there would be significant conversion of the DNT to DAT in the absence of electric current. It is common in chemical engineering to reduce DNT to DAT using hydrogen, but usually using a catalyst and high temperature. These experiments were conducted in the same manner as the oxygenated experiments. These experiments were conducted with the graphite rod and a titanium mesh cylinder as the cathode. Hydrogen gas was bubbled into the reactor with no current applied. This resulted in no measurable degradation of DNT, indicating that current is necessary.

Table 12. Mass balance with the titanium mesh wire cathode, at 2500 rpm, oxygenated.

Current (mA)	Compounds	Solid Phase (% Molar Conversion of DNT to)	Aqueous Phase (% Molar Conversion of DNT to)
65	DAT	—	55.5
	D-2	32.2	—
	Total	32.2	55.5
Total Mass Balance (% Molar Conversion of DNT to identified products) = 87.7 %			
45	DAT	—	34.2
	Nitroso-1	—	11.0
	D-1	5.2	—
	D-2	45.5	—
	Total	50.7	45.2
Total Mass Balance (% Molar conversion of DNT to identified products) = 95.9 %			
23	DAT	—	26.7
	Nitroso-1	—	5.5
	AN-1	—	8.9
	D-1	8.2	—
	D-2	34.4	21
	Total	42.6	62.1
Total Mass Balance (% Molar conversion of DNT to identified products) = 105 %			

Table 13. Mass balance with the titanium mesh wire cathode, deoxygenated.

Current (mA)	Stir rate (rpm)	Dissolved Oxygen	DAT Conc. in ppm* (% Molar Conversion of DNT to DAT)
23	540	0.2	24.7 (74.7)
23	2500	0.2	31.0 (93.0)
45	540	0.2	26.2 (92.0)
45	2500	0.2	26.7 (93.0)
65	540	0.2	24 (77.0)
65	2500	0.2	24 (78.0)
* Note that due to the different extents of degradation of 2,4-DNT at the end of each experiment, the percentage values are not comparable from one experiment to the next.			

4 Discussion

The study of electrochemical degradation of DNT was conducted to determine if the process would proceed abiotically. This is of interest in DNT treatment because the biological transformation of DNT under aerobic conditions has been shown to be sensitive to the presence of other compounds (Freedman et al. 1996), but the transformation of DAT was not impeded by the presence of those compounds. Thus, the mineralization of DNT appears to rely on a two-step process (Maloney et al. 1992). The aerobic step is usually available at Army industrial facilities (e.g., an industrial wastewater treatment plant). However, the anaerobic step necessary to convert the DNT to DAT, using an easily degradable co-substrate to maintain anaerobic conditions, would have to be installed as a pretreatment at the source of the wastewater. Production schedules for items containing DNT as a component are such that there is not a consistent flow of wastewater containing DNT. However, the biological process would have to be maintained in a stable, active condition for times that DNT is in the wastewater.

Maintenance of a stable, active biomass requires feeding nutrients and substrate to the process, which can become a significant cost when the production process is shut down for long periods. This is a particularly important concern in the current production schedule, where there are relatively small requirements for materiel that generates DNT contaminated wastewater. The biological process would have to be maintained in an "idle" status, but would incur costs from feeding substrate and nutrients.

The aerobic biological process is always available, as there are many other sources of wastewater than the DNT-contaminated wastewater. Thus, the requirement for maintaining the active biomass in the anaerobic process would be removed if the conversion of DNT to DAT could be performed in an abiotic manner.

The results obtained here indicate that the conversion can be effected abiotically in an electrochemical reactor. Process economics have not yet been determined, but this abiotic process may be more cost effective where long downtime periods are expected in the production schedule.

The results also point to a potential secondary mechanism of DNT removal, in terms of polymerization of the contaminants to form insoluble precipitates. The

precipitates accounted for up to 70 percent of the influent DNT in the studies reported on here. This technique has been evaluated previously (Alberti and Klibanov 1981) using enzymes and hydrogen peroxide. Alberti and Klibanov also showed the importance of having aromatic amines available to initiate the polymerization. In their studies, nitrated aromatic compounds did not react with the enzyme and hydrogen peroxide to produce polymerized products, but in the presence of aromatic amines, the precipitation reaction occurred.

The data in this study indicate the precipitation reaction can occur as long as oxygen is present at the time of the reductive transformation. The major dimers observed were products of reaction at the amino group. The resultant compound is then removed from the aqueous phase as a precipitate, although some of the dimer is found in the wastewater. The advisability of deliberately using the precipitation mechanism is not currently known, as there is no toxicity data on the dimers. However, the partially reduced by-products of DNT are found in the effluent of the wastewater treatment plant at Radford Army Ammunition Plant, so it is likely that the dimers are already being formed in the aerobic environment of the secondary treatment process.

The studies reported on here were conducted under highly controlled conditions in which purified compounds were evaluated in bench scale reactors. Further work is required on the effects, if any, of other contaminants expected to be found in the wastewater containing DNT, most notable ethanol and ether. A cost comparison can then be performed to determine if and when the use of an electro-chemical reduction process may be more cost effective than an anaerobic biological process.

5 Conclusions and Recommendations

The research shows that electrochemical reduction of 2,4-DNT takes place readily in the reactor. The products of the electrochemical degradation are 2,4-DAT in deoxygenated experiments and a complicated mixture dominated with the azoxy dimers in oxygenated experiments. In oxygenated systems, a large fraction of the products is present in the form of precipitate rather than in the aqueous phase. The stirring rate only influences the overall rate of degradation at currents of 53 and 65 mA and only with the graphite cylinder. The available surface area of the cathode has a linear effect on the rate of degradation of 2,4-DNT.

The electrochemical reduction of 2,4-DNT can be used to transform it effectively. The products are quantified and found in both the aqueous phase and the precipitated solid formed during the degradation of 2,4-DNT. Therefore, any scale-up process must be able to deal with the solids formed. It is recommended that different electrode configurations be tested before the technique is applied in the field. Experiments with a lower salt concentration more representative of Army wastewaters should be carried out. Additionally, experiments with a flow-through reactor should be done since the batch mode operation studied here will not be the likely mode of operation in the field.

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13. ABSTRACT *(Maximum 200 words)*

This study evaluated electrochemical reduction of a model nitro aromatic (dinitrotoluene, or DNT) that has shown the tendency to undergo reduction reactions. Objectives were to investigate the effect of stirring rate and the identity of the cathode material on the rate of DNT degradation, and to evaluate the fate of by-products, with specific attention to the mass balance and the potential formation of polymers of the reduced compounds and the parent compound. A bench-scale study was done of the degradation of 2,4-DNT in an electrochemical reactor. The rate of the degradation was measured under various experimental conditions. The by-products of degradation were identified by gas chromatography-mass spectrometry (GC-MS) and GC. A mass balance for the products was obtained under a variety of experimental conditions, both in the aqueous and solid phases. The stirring rate was found to affect the overall rate of degradation in some cases. A satisfactory mass balance for the products was achieved with 2,4-diaminotoluene (DAT) dominating in deoxygenated experiments and the dimers being important in the precipitating solid in the oxygenated experiments.

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