Carbon nanotube catalysts: an approach toward nanodimensional reactions

Mindy Gordon

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Carbon Nanotube Catalysts: An Approach Toward Nanodimensional Reactions

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July 2003

A thesis submitted in partial fulfillment of the requirements for the degree of

Master of Science in Chemistry

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Abstract

The oxidations of aromatic and aliphatic amines have been investigated to evaluate the catalytic effect of functionalized multiwalled carbon nanotubes. Aniline oxidation by hydrogen peroxide produces very low yields of azoxybenzene; similarly, $p$-toluidine oxidation produces azoxytoluene after long time periods. When functionalized multiwalled carbon nanotubes are present in these reactions, the above oxidations produced unique products such as azobenzene or azotoluene within a short period. The course of the reaction has been followed by GC/MS that showed a mass number of 198 corresponding to azoxybenzene (without carbon nanotubes) or 182 corresponding to azobenzene (with the nanotubes). The first stage of the oxidation is identified as nitrosobenzene formation which subsequently couples with the parent molecule to produce the azo compound. UV-VIS absorption spectroscopy showed no peak in the absence of the carbon nanotubes; in contrast to a distinct peak at 347 nm when the reaction is catalyzed by carbon nanotubes. The GC/MS data for the $p$-toluidine oxidation showed a mass spectral peak at a mass number of 226, corresponding to azoxytoluene, which is replaced by 210, corresponding to azotoluene, when the reaction is catalyzed by the nanotubes. In agreement with the above results,
the UV-VIS absorption data showed an azotoluene peak at 464 nm.

To reduce the unwanted product contribution coming from the outer solution, a carbon nanotube column was configured. In this situation 100% azobenzene formation was obtained when aniline was oxidized. The efficiencies of the different columns range from 50-97% for the \( p \)-toluidine oxidation reaction. The oxidations of diphenylamine and methylamine have also been carried out in the column configuration to understand the mechanisms. The results suggest the feasibility of constructing a nanosynthetic machine for generating high yields of products in the above reactions.
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Posters/Presentations


M. Croston and K.S.V. Santhanam, *Concept of Nanosynthetic Machine with Functionalized Carbon Nanotubes*, poster, ACS meeting – Rochester division, October 2002
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1. Introduction

The synthesis of fullerenes and carbon nanotubes may be considered as one of the important discoveries of the 20th Century. Kroto, Curl and Smalley (1) pioneered the effort when they began studying a new allotrope of carbon called the fullerene. Another turning point in the history of the chemistry of carbon came with the discovery of the tubular structure of carbon by Iijima [2], which is rapidly being investigated for material structure, strength and catalytic properties. This thesis is devoted to the unprecedented study of catalytic properties of carbon nanotubes in organic oxidative reactions which may be amenable for the construction of nanosynthetic machines for organic preparations.

1.1 Structural Aspects of Carbon

There are four different types of graphite structures that will be discussed: diamond, planar graphite, buckminsterfullerenes and carbon nanotubes. Diamond exists as a face-centered cubic unit cell consisting solely of carbon atoms. Planar graphite consists of planes of carbon atoms arranged in hexagons which layer each other. Graphite seems to be “slippery” because the planes can be easily separated from and moved across each other. This is why graphite is used in pencils. The buckminsterfullerene is spherically shaped with the carbon ends forming a pentagon to close the sphere. Nanotubes are formed in somewhat the same fashion, either single or multiple graphitic planes are rolled into a tube with carbon pentagons existing as the end caps.
1.1.1 Graphite (amorphous)

Graphite bonding is $sp^2$ hybridized and exists as a flat plane and has a 3-fold coordination system [3].

1.1.2 Diamond

Whereas graphite is $sp^2$ hybridized, diamond exists as $sp^3$ hybridized carbon in a four-fold coordinated structure [3]. The C-C bond distance for diamond is larger than that of graphite due to the weaker forces between the atoms [3].

1.1.3 Carbon Nanotubes

Multiwalled carbon nanotubes have diameters from 10-50 nm and can be 10 μm in length or longer. Multiwalled nanotubes have a density of 1-2 g/cm$^3$ and a very large surface area of 10-20 m$^2$/g. Single walled nanotubes have diameters of 1-1.4 nm and can be as long as 100 μm. Whereas multiwalled nanotube bundles are straight, single walled nanotube bundles are curled and looped. Carbon nanotubes can exist in three different orientations that affect their electrical properties: zigzag, armchair and chiral, or helical [4]. Zigzag nanotubes can either act as semiconductors or metals, armchair tubes are mainly semiconductors and chiral tubes are primarily metallic. One of the most promising characteristics of carbon nanotubes, other than that they can be conducting is that they can be ballistic conductors, which means that there will be no scattering of electrons [5]. They also have the highest current density of any known material at $10^8$ A/cm [6]. Carbon nanotubes are approximately 100 times stronger than steel with a strength of 60,000 psi. They are also very light with a density of 1.33-1.4 g/m$^3$ [7].
Nanotubes can be very elastic having a Young’s Modulus of 1500 GPa [7]. They also have a high thermal conductance, which has been measured at ~2000 W/mK at room temperature [8] and, they have electrical conductance properties comparable to that of copper (5.9x10^7 Ωm) [9]. When nanotubes are made, they form bundles of themselves that contain all three orientations of the nanotubes. Researchers at IBM have developed a method of separating the metallic CNT from the semiconducting CNT for use in single carbon nanotube transistors [10].

1.1.4 Synthesis of Carbon Nanotubes

There are now many different ways in which carbon nanotubes can be synthesized. The single walled tubes are generally made by laser ablation of a graphite rod using a nickel or palladium metal catalyst. MWCNTs are generally prepared by the carbon arc method in the presence of helium or hydrogen gas. In this case, no metal catalyst is needed.

Figure 1. MWCNT carbon arc setup.¹¹
The carbon arc method for producing nanotubes is shown in Figure 1 [11]. The cathode and the anode are housed in a double-walled water-cooled condenser. When a 20-25 V DC arc current is passed across the anode to the cathode in the presence of 30-500 Torr of H₂ or He₂ gas, at 2500-3000 °C, the cathode length begins to decrease and CNT are formed [11]. Soot is collected down at the bottom of the vessel. The cathode is removed and the multiwalled carbon nanotubes are collected. MWCNT can also be formed by pyrolysis.

![Figure 2. Apparatus for the preparation of MWCNT by pyrolysis.](image)

This apparatus shown in Figure 2 consists of a quartz tube with an inner diameter of 20 mm and a heating zone of 200 mm [12]. Acetylene is passed through a liquid Fe(CO)₅ bubbler at 300 sccm using argon as a carrier gas flowing at 30 sccm [12]. The gases and the catalyst are then introduced into the quartz tube and heated at 750-950 °C for 30 minutes [12]. The furnace is then cooled to room temperature at an Ar flow rate of 500 sccm [12]. The nanotubes are then collected. SWCNT can also be produced by the arc discharge method. In this case, however, a metal is mixed with the graphite of the anode.
This metal can be in the form of Co, Co/Ni, Co/Y, Co/Fe, Ni/Y, Ni/Fe with Ni/Y giving the best results. These catalysts promote the growth of the single walled structures. The most common method of preparing SWNTs is by laser ablation. Figure 3 shows the laser ablation apparatus, which consists of a 60 cm long quartz tube with an outer diameter of 3.6 cm and an inner diameter of 2.7 cm [12]. A target (~5μm in diameter) consisting of a compressed graphite, Ni and Co powder is placed inside the quartz tube at a temperature of 1200 °C [12]. Argon gas is introduced into the quartz tube at a rate of 0.2 L/min and a pressure of 700 Torr. A Nd:Y pulsed laser beam is then shown onto the target and bombards the target surface with 150 pulses of light [12]. The laser has a wavelength of 532 nm with a pulse width of 6-7 ns and a frequency of 10 Hz [12]. The beam current is 2 J/xm² with a diameter of 2 mm [12]. Once the laser ablates the target, the nanotubes are collected on a water-cooled copper collector.

\[\text{Figure 3. Laser ablation apparatus for the preparation of SWNTs.}^{12}\]

SWNTs can also be made by a chemical vapor deposition (CVD) process. In this case,
an iron oxide catalyst is prepared. Methane is decomposed in a furnace at 1000 °C in the presence of the iron oxide catalyst [12]. The iron oxide catalyst is prepared by impregnating alumina nanoparticles in methanol with Fe(NO₃)₂·9H₂O at room temperature for 1 hr [12]. The solvent is then evaporated at 80°C and the catalyst is then heated and ground into a powder. The alumina/iron oxide catalyst is then placed in a quartz tube and heated at 1000 °C with an Ar flow [12]. Methane is then introduced into the quartz tube at a flow rate of 6150 cm³/min at 1.25 atm pressure [12]. After 10min, the methane is then purged by reintroducing Ar [12]. The CVD process has been studied to provide the optimum conditions for CNT growth. Other carrier gas/catalyst combinations have been used including n-hexane/ferrocene thiocene used at RPI [13].

1.1.5 Structural Representations

Single-walled and multi-walled carbon nanotubes are shown in Figures 4 and 5. Single-walled nanotubes consist of carbon atoms arranged in a hexagon and rolled into a tube. The multiwalled carbon nanotube in Figure 4 consists basically of concentric single-walled nanotubes.

Figure 4. Single-walled carbon nanotube.¹⁴
Figure 5. Multi-walled carbon nanotube.15

If the nanotube in Figure 5 was opened and laid on a flat surface, it would look like Figure 6 (a and b), a flat graphene sheet. Figure 6 (b) shows how the helicity of a carbon nanotube is determined.

Figure 6. Helicity of a carbon nanotubes.11
The helicity is defined by the m and n indices in parentheses on the diagram (n,m) [11]. When m and n are equal, the nanotubes are said to be in armchair [11] configuration. When m is equal to zero, the nanotubes are considered to be zigzag [11]. If n and m are different from each other and m is not equal to zero, the nanotubes are chiral [11]. All armchair nanotubes are metallic as shown on the diagram and zigzag tubes can either be metals or semiconductors [11].

Figure 7. Helicity of carbon nanotubes.¹¹

Figure 7 shows nanotubes of different helicities: (a) represents an armchair nanotube, (b) represents a zigzag nanotube and (c) represents a chiral nanotube [11]. Armchair and
zigzag tubes are perfectly symmetrical throughout the nanotube whereas chiral tubes are not as can be seen in Figure 7 [11]. When nanotubes are formed, they have endcaps on both ends of the tube. Once they are purified, the endcaps are broken off as is shown in Figure 7. This concept will be discussed in more detail in an upcoming section.

1.2 Electrical Properties

Carbon nanotubes can act either as metallic or semiconducting tubes depending on their geometry. For typical metallic systems, electrons can move from one metal to the next quite easily. In the case of CNT, however, because they possess such different electrical properties, electrical current will not always flow easily from one tube to the next [3]. Introducing a Schottky barrier into the nanotube (bending the nanotube at one point), allows the flow of electrical current to continue [3]. Nanotubes possess these defects when they are made and they can also be formed by inducing a rotation of bonds between two hexagons to form a five-fold ring and an adjacent seven-fold ring [3]. This allows a single nanotube to possess both semiconducting and semi-metallic character [3].

1.3 Mechanical Properties

Carbon nanotubes have excellent mechanical properties due to their low density of defects [16]. The Young’s modulus of CNTs (reported previously) is higher than tubes composed of other atoms [16]. This value only slightly depends on the diameter of the nanotubes and depends on the degree of $sp^2$ hybridization [16]. The Young’s modulus is highest for a flat graphene sheet due to the fact that folding the sheet into a nanotube would distort $sp^2$ hybridization [16]. As with the Young’s modulus, the Poisson
ratio (v) of a nanotube also depends on its diameter, but is dependent on chirality as well [16]. Planar graphite has a Poisson ratio of \( \nu = 0.17 \), armchair tubes have a \( \nu = 0.14 \), and other chiralities range from \( \nu = 0.18-0.19 \) [16]. When stress is applied to nanotubes, both thin and thick-walled nanotubes exhibit compressive strengths one order of magnitude higher than any known fiber [16]. Zigzag and armchair nanotubes are the stiffest at 0 K [16]. Nanotubes are also very flexible [16]. When subjected to large amounts of deformation, the nanotubes switch into different shapes releasing energy [16]. This can be reversed and is caused by the ability of sp\(^2\) hybridized C-C bonds to reversibly change hybridization, to sp\(^3\) in this case, when deformed out of a plane [16].

1.4 Purification and Functionalization of Carbon Nanotubes.

There are many different methods for purifying and functionalizing CNTs. No matter what method is used to produce MWNT or SWNT, the soot is not 100% nanotubes. As a matter of fact, the purity of the sample can be between 10-90%. The CNTs in the sample come in three different forms. They can either be completely closed tubes, have one end open or have both ends open. The purpose of purifying the CNTs is to remove most or all of the excess amorphous graphite material and to open both ends of all of the nanotubes that are present. This is usually done in the presence of a strong acid for approximately 12 hrs. The acids involved can be hydrochloric, nitric and sulfuric acid. In most of these cases, the ends are opened by oxidating the carbons in the pentagon rings of the endcaps as they can be easily oxidized due to their geometry. When this occurs, carbonyl groups can be found at the dangling carbon bonds left on the ends of the tubes. Thermal annealing in oxygen also opens the endcaps of nanotubes
Figure 8. Apparatus for the thermal annealing of CNTs.\textsuperscript{17}

The apparatus in Figure 8 represents one that is used to purify the nanotubes by thermal annealing. The cathode deposit is placed in the inner tube of the furnace and is constantly rotated at 30 rpm. The temperature is fixed at 760 °C throughout. In this case, most of the carbonaceous material was removed and the weight was reduced to 40% of the original \textsuperscript{17}. Purification of MWNT by intercalation of CuCl\textsubscript{2} \textsuperscript{18} has also been reported. Nanotubes can also be purified and oxidized using ozone \textsuperscript{19}. In gas-phase ozone oxidation, CNTs are placed into a vertical reactor containing a mixture of ozone and oxygen gases and heated at 150-200 °C for 30-90 min \textsuperscript{19}. Liquid phase oxidations performed by suspending the CNTs in an acidic solution (ClO\textsubscript{4}\textsuperscript{-}, MnO\textsubscript{4}\textsuperscript{2-} or H\textsubscript{2}O\textsubscript{2}) along with the oxygen/ozone gas mixture and heated at 60-70 °C for 24 hrs \textsuperscript{19}. In both of these cases, the endcaps, and any kinks or steps that may occur in the nanotubes themselves, are the first to be oxidized and the bonds broken. Other purification methods include irradiating the nanotubes in an infrared radiation heating system \textsuperscript{20}. 
Figure 9. Irradiation apparatus for purifying nanotubes.\textsuperscript{20}

Figure 9 shows the apparatus for this type of purification. The cathode deposit from the carbon arc method is placed directly in the path of the infrared beam. Here, it is irradiated for 30 min at 500 °C in air. The product was a spongy square of MWNTs with a surface area of 10 mm\textsuperscript{2} and 0.1 mm thickness [20].

1.4.1 Chemical Properties

The chemical properties of carbon nanotubes are now being extensively explored. Only one end of a carbon nanotube is open as it exists after it is made. The other end can be opened, exposing the nanotube to the possibility of filling it with molecules thereby acting as a vessel. They also have a high specific area which suggests that many molecules can be adsorbed onto the surface of the tubes. As the nanotubes are opened, they can also be functionalized – other molecules can be introduced to the ends of the carbon chains. Carbon nanotubes can also act as electrodes, increasing the rate of electrochemical reactions [21].
1.4.2 Applications

The potential applications are numerous based on the extraordinary electrical and mechanical properties that carbon nanotubes possess. Some recent advances and important research areas are discussed here.

It has been noted that CNTs have the ability to conduct water by capillary action, the same way that kidneys and other small blood vessels move water [22]. There are two major implications here. First, nanotubes would be extremely valuable in biological systems. This provides the potential for artificial organs, such as kidneys, and recently, scientists have been determining whether CNTs can be used as artificial muscles [23]. This also implies that CNTs can act as carrier vessels or "nano test tubes". Small molecules in solution can enter into the CNTs, as has already been shown by de Heer, et al. CNTs were filled with gaseous or solution-phase metals which were decomposed to solid metals inside the CNTs [24]. CNTs can also be used in transistors and diodes. They are very small and the electronic properties are perfect for these types of devices because electrons can move freely within them with little or no scattering. IBM has recently developed a transistor using a single carbon nanotube gate [10].
They can also be used as field emitters for flat-panel displays. Many scientists, recently, have been testing nanotube/polymer composites. Nanotubes have superior mechanical properties compared to polymers, so the addition of CNTs should provide increased strength and hardness. They have also been added to conducting polymers to increase the electrical properties of the polymers.

In the US, we are always looking for ways to increase energy efficiency and to eliminate pollution. Recently, the president has granted a bill that provides money for hydrogen fuel cell research. CNTs play a big role in this category. They have been shown to be highly efficient for the storage of hydrogen gas. A single gram of carbon nanotubes can absorb $>3$ wt% hydrogen under 290 K and $\sim$10 MPa [25] which is potentially useful for fuel cell applications. Purified MWNTs have also been used to electromechanically catalyze oxygen reduction in fuel cells. Batteries can be made using CNTs that will have an improved lifetime over traditional metal catalyzed batteries [26].

Another possible application of CNTs is to use them as biosensors for harmful
gases or for chemical analysis. Conducting polymer/CNT composites have already been used in gas-detection sensors. The hope is that we will be able to use CNTs in a very small apparatus that could be remotely operated to areas where humans may be in harm. These small sensors could easily be undetected and could transmit information regarding the purity of the air or water.

CNTs can also be used in microscopy. Recently, atomic force microscopes have been developed that use a carbon nanotube as a tip rather than a gold electrode [27]. We are moving toward smaller dimensional particles and we need to be able to analyze surfaces in the smallest dimensions. Using a single carbon nanotube at the tip of an AFM allows us to analyze surfaces on the order of nanometers, which has never been done before. Thus the foundation for the development of nanoscience has emerged.

1.5 Nanoscience

Nanoscience is most widely defined as the phenomenon associated with structures roughly in the 1-100 nm range where the properties are of interest due to the size of the structure, and are typically different than those of a molecule or a comparable bulk material. We plan to prove that when a reaction is confined to nanodimensional carbon structure, the products are different than in the bulk solution. Basically, any chemical object of submicrometer dimensions or with submicrometer features can be considered a part of nanoscience.

Why is nanoscience important? When matter is confined to a small space, as will be proven in this thesis, phase transitions can occur that cannot be observed in larger systems. In today’s information age, smaller particles and devices can mean faster chips.
This will allow us to get information faster than ever. Resist layers may be deposited monomolecularly which will allow for the smallest devices possible. Research in nanoscience has allowed for the development of conducting polymers as thin film transistors.

Chemical applications in nanoscience include building molecules from the bottom up. We may be able to build a molecule piece by piece with specific stereochemistry. The possibility of developing monodisperse assemblies of clusters to form high molecular weight units has also been realized.

1.5.1 Nanodimensional Reactions

A nanodimensional reaction is defined as a reaction that occurs in a space where at least one dimension is less than 1 μm. When a reaction is confined to a very small space, the molecules are forced to react with each other where they would not ordinarily do so. This allows for different products in the nanoscale than would be formed in the macroscale. In this case, a reaction is confined within a carbon nanotube.

![Figure 11](image)

**Figure 11.** Reaction inside a carbon nanotube.

Figure 11 represents a nanodimensional reaction. Here, molecules A and B are in
solution and diffuse into the carbon nanotube through two forces. First, the solution is being pulled into the tube by capillary action. Secondly, the light-colored spots located on the inside of the CNTs represent electron densities on the nanotube.

Electron densities are present anywhere on the nanotube where a kink or step is found, or where the nanotube bends for any reason. They are charges that build up on the surface or within the nanotube that occur during the synthesis of the nanotubes. These electron densities are negatively charged and they help to attract the partially positive charges on the molecules and hold them until they can react with other molecules present. Hertel, et al. showed that carbon nanotubes can be manipulated by an AFM tip, that is, they can be bent at the point where the electron densities occur in the nanotubes [28].

1.6 Purpose of the Thesis

The purpose of this thesis is threefold. The first is to examine the catalytic nature of the multiwalled carbon nanotubes in organic oxidative reactions where the reactants, intermediates and products are present in the confined tubular topology of carbon nanotubes containing flexible electron densities. For this purpose, the chemical oxidations of primary and secondary, aromatic and aliphatic, amines have been chosen as they form an important class for producing conducting polymers through a colored intermediate species. The monitoring of any chemical reaction within the nanotube directly is an uphill task except in situations where the product is deposited as a solid metal and can be analyzed by Transmission Electron Microscopy [24]. As it is impossible to determine whether reactants are situated inside a nanotube, there has not been any report yet in the literature of studying chemical reactions inside the carbon
nanotubes. If a reaction produces a colored product inside the carbon nanotube, then its diffusion into the outer solution could be monitored by optical absorption spectroscopy. As this is generally a slow process, a time dependent absorption profile is to be expected in the above oxidative reactions.

The second aspect of this study is to examine the synthetic schemes in the oxidation of amines, such as aniline and p-toluidine, when carbon nanotubes are present.

The third aspect is to study the effect of a column configuration of carbon nanotubes on the product yield in the above oxidations, and, to compare its performance to carbon nanotubes suspended in the medium. When the carbon nanotubes are arranged in a column configuration, the reactants are continuously in contact with the carbon nanotubes. This reduces the interference arising from the oxidative reactions occurring in the suspended medium.

The multiwalled nanotubes used in the oxidation of the above amines are purified and functionalized using a modified method of Green, et al. [29]. They are analyzed and characterized by FTIR, SEM, TEM and TGA. The products obtained in the oxidation of amines are analyzed, characterized and determined by UV-VIS, GC/MS, Fluorescence and FTIR. Based on the analytical data, the reaction and kinetic mechanisms are determined. The results point to the feasibility of constructing a carbon nanotube-based synthetic machine.
2. Experimental

2.1 Chemicals

*p*-Toluidine and methyamine (41% in water) were purchased from Aldrich and used as received. Aniline (Aldrich) was purified by distillation. The sample was collected at 180°C, sealed and kept under refrigeration until further use. Azobenzene was purchased solid from Aldrich and kept in a dessicator until use. Hydrogen peroxide (30% vol/vol) (Baker Analytical grade) was kept under refrigeration and used in all of the experiments. All solvents were Baker Reagent or Analytical grade and used as received. Nitric acid (69.0-70%) (Baker Analyzed ACS Reagent) was used in the functionalization of the nanotubes. Fisher Scientific Decolorizing carbon (Norite) was used as the active carbon sample.

2.2 Instrumentation

2.2.1 UV-VIS Analysis of the Reaction

All reactions were monitored using a Shimadzu UV2000 series spectrometer. The method parameters for the instrument were as follows: wavelength = 200-800 nm scan, slit width = 0.5 mm, scan speed = medium. A quartz cuvette was used for all experiments. All experiments were performed using the solvent as the blank.

2.2.2 GC/MS Characterization of the Products

The reactions were monitored using a Hewlett-Packard GC-MS (HP6890 series
with HP 5973 mass selective detector and fitted with an Agilent (19091S-396) column. The GC column used prior to January 2002 was an HP-1MS (100% dimethylpolysiloxane) which had capillary measurements of 60 m x 250 μm x 0.25 μm nominal. The column used after January 2002 was an HP SPB-5 (5% Phenyl, 95% Polysiloxane) which had capillary measurements of 15.0 m x 200 μm x 0.20 μm nominal. A standard method was used with this column when determining the formation of different azo groups. The injection temperature was set at 280 °C and helium gas flowed at a rate of 1 mL/min with the flow rate of the column set at 2.2 mL/min. The column temperature was set at 80 °C for 1 minute, then increased to 220 °C at a rate of 20 °C/min and then increased to 280 °C at a rate of 4 °C/min. The injection of the sample ranged from 1 to 5 μL.

2.2.3 FTIR of Carbon Nanotubes and the Products

Infrared spectra were determined using a Bio-Rad FTIR spectrometer (Excalibur Series). Solid samples were analyzed using a diffuse reflectance attachment. Multiwalled carbon nanotubes were ground in KBr and kept in the powder form during analysis. Liquid samples were placed between two KBr salt plates and placed directly in the path of the infrared beam.

2.2.4 TGA of Carbon Nanotubes

The carbon nanotube samples were analyzed for their thermal degradation temperatures using a Universal TA TGA Instrument (model V2.6D). Samples were heated both in air and in nitrogen up to 900 °C.
2.2.5 Fluorescence Spectra of Azobenzene and the Products

A Perkin-Elmer Luminescence Spectrometer LS50B was used to determine the fluorescent properties of azobenzene, aniline, acetonitrile and acetone.

2.2.6 Atomic Absorption of Carbon Nanotubes

The carbon nanotubes were sonicated in a nitric acid solution and analyzed for Cu and Fe content using a Perkin-Elmer AAnalyst 100 atomic absorption spectrometer.

2.2.7 pH of the Carbon Nanotubes

The carbon nanotubes were sonicated in water and analyzed using a VWE pH meter Model #8005 with Accumet glass and reference electrodes.

2.3 Procedures

2.3.1 Functionalization of Carbon Nanotubes

Multiwalled carbon nanotube core material was purchased from DEAL International, Nanotechnology Division. To functionalize, open and purify the carbon nanotubes, 2 g carbon nanotube core material were suspended in 43 mL concentrated nitric acid and refluxed for 12-24 hrs. at a temperature of 140 °C. The nanotubes were then washed several times with distilled water and then refluxed in distilled water at 100 °C for approximately 5-10 hrs. The nanotubes were then filtered and dried overnight in a 100 °C oven. Multiwalled carbon nanotubes were also received from Rensselear
2.4 Oxidation of Aniline.

Aniline and hydrogen peroxide were reacted together in acetonitrile, acetone, hexane or methanol in the presence of functionalized CNT, nonfunctionalized CNT, activated charcoal and graphite in a honeycomb sheet received from Prof. D. D. L. Chung at the University of Buffalo. The reactions were performed at room temperature and at 40 °C for comparison. Various amounts of CNT were added to the solution for kinetic studies. Upon formation of the simulated nanomachine, a solution of aniline, hydrogen peroxide and solvent was mixed and added dropwise to the CNT column. The products were analyzed by GC/MS and UV-VIS in all cases and by Fluorescence spectroscopy in some.

2.5 Oxidation of p-Toluidine.

p-Toluidine and hydrogen peroxide were reacted together in acetone or acetonitrile in the presence of functionalized carbon nanotubes and varying amounts of nonfunctionalized CNT. A control solution was made that contained only the two reactants and solvent for comparison. All reactions were performed at room temperature unless otherwise noted. Upon completion of the simulated nanomachine, the solution was prepared and then introduced into the CNT column dropwise. The products in all cases were analyzed by GC/MS and UV-VIS absorption spectroscopy.
2.6 Oxidation of Methylamine.

A 1:1 ratio of methylamine to hydrogen peroxide solution was prepared in acetone and acetonitrile in the presence of functionalized CNT. A control solution was also made for comparison that contained no CNT. Upon preparation of the simulated nanomachine, the solution was prepared in a test tube and then introduced into the CNT column dropwise. The products in both cases were analyzed by GC/MS and UV-VIS.

2.7 Oxidation of Diphenylamine.

A 1:1 solution of diphenylamine to hydrogen peroxide in acetonitrile was prepared. This solution was then added dropwise to the functionalized CNT column and the product obtained was analyzed by GC/MS and UV-VIS spectroscopy.

3. Results and Discussion

3.1 Characterization of Carbon Nanotubes.

3.1.1 Fourier Transform Spectroscopic Studies

Multiwalled carbon nanotubes were analyzed using the FTIR spectrometer before and after functionalization to determine whether there is a change in functional groups during the process. Figure 12 shows the IR spectrum before the tubes were functionalized.
Figure 12. FTIR spectrum of carbon nanotubes prior to functionalization.

It can be noted that no carbonyl peak (1600-1800 cm\(^{-1}\)) can be observed in this spectrum. The peaks are rather weak in this spectrum due to the reflection of the light scattering off of the nanotubes. However, when comparing this spectrum with the Figure 13, there is a significant peak difference after functionalization.

Figure 13. FTIR spectrum of carbon nanotubes after functionalization.

A peak is present at 1880 cm\(^{-1}\) after functionalizing the carbon nanotubes which indicates a strained carbonyl group. The functionalization of the nanotubes not only opens the
nanotubes, but it oxidizes some of the end groups and defect centers to carbonyl groups.

3.1.2 Thermogravimetric Studies

The nanotubes before and after functionalized were analyzed by thermogravimetric analysis to determine whether the degradation temperature and characteristics change during functionalization. Figure 14 shows the TGA graph of the core ground material as received. The material begins to degrade in the range of 560 to 720 °C. 100% of the starting material (3.865 g core material) was degraded under air flow.

![TGA graph of CNT prior to functionalization](image)

**Figure 14.** TGA graph of CNT prior to functionalization.

Figure 15 shows the TGA of the sample after functionalization. In this case, the CNT
shows a phase transition at approximately the same temperature, 580 °C, but does not finish degrading until almost 900 °C, a difference of almost 200 °C. There is no residue left in this experiment. This difference could be due to the carbonyl end groups that have been acquired during functionalization. It would be harder to oxidize the carbonyl groups than to oxidize pure carbon, causing the breakdown of the carbon nanotubes to take a longer time, providing a longer range of degradation in the TGA data. The spectra clearly show a difference between the two samples of CNT.

![TGA spectrum of CNT after functionalization](image)

**Figure 15.** TGA spectrum of CNT after functionalization.

### 3.1.3 Scanning Electron Microscopic Results

The carbon nanotubes were taken to RPI (Troy, NY) to be analyzed by SEM and determine what the content of the material was. Figure 16 shows the SEM image of the carbon nanotubes after functionalization. The image shows mostly large masses of gray material which represent compressed nanotube bundles, and some large spikes of carbon.
nanotubes. This analysis shows that the carbon nanotube bundles were present after purification. The samples from RPI were relatively non-bundled and showed separated tubes.

Figure 16. SEM image of functionalized carbon nanotubes.

3.1.4 Transmission Electron Microscopic Studies

The carbon nanotubes were then analyzed under a transmission electron microscope also at RPI to determine the characteristics of the nanotubes, i.e., whether they were opened, whether defect centers were present, and what changes may have occurred in the end groups of the nanotubes during functionalization.
Comparing Figures 17 and 18 provides important information regarding the change of the CNTs after functionalization. Before functionalization, the nanotubes have a closed end, the pointed end of the nanotube in Figure 17. In both figures, the hollow center of the nanotube can be seen and the many layers of the multiwalled nanotube are visible. After functionalization, Figure 18, the endcaps of the nanotubes have been broken, or cleaved,
off. The nanotubes have also been broken in some places by the nitric acid.

3.2 pH of Carbon Nanotubes

To ensure that there was no nitric acid left on the nanotubes, 60 mg of functionalized CNT were placed in distilled water and sonicated for 1 hr before being analyzed for the pH of the water. It is assumed that after 1 hour of sonication, any nitric acid that may be adsorbed onto the surface or may have diffused into the nanotubes will be removed and left in the water solution. Table 1 gives the values from this experiment. It is obvious from these results that there is no nitric acid left after the washing process from functionalization of the tubes. The overall result is a solution that is slightly more basic than distilled water.

<table>
<thead>
<tr>
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<th>pH of buffer solution (7.00)</th>
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<th>pH of CNTs sonicated in water</th>
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<td>7.51</td>
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</tr>
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</tr>
<tr>
<td>Std. Dev.</td>
<td>4.47E-03</td>
<td>1.92E-02</td>
<td>4.38E-02</td>
</tr>
</tbody>
</table>

3.3 Atomic Absorption of Functionalized Carbon Nanotubes

The nanotubes were sonicated in a nitric acid solution and analyzed by AAS for copper and iron content. Neither of these metals was detected during these experiments.
3.4 Oxidation of Primary Amines

3.4.1 Aniline-Discovery of the Effect of Carbon Nanotubes

The initial experiments were performed with 1 M aniline and 1 M hydrogen peroxide in 25 mL of acetonitrile (control solution) in a reflux at 60 °C for 3 hours. After the first hour, the solution began to turn a light yellow color and after the second, a darker yellow color. At this point, no carbon nanotubes had been added. The solution was analyzed by GC/MS and the major peaks seemed to be aniline, acetonitrile and carbon dioxide although nitrobenzene and nitrosobenzene were also formed after 24 hours. Carbon nanotubes were then added to a different 1 M aniline and 1 M hydrogen peroxide solution and refluxed for 3 hours at 60 °C. At the end of the three hours, the solution was a deep red in color (see Figure 19). Due to the color of the solution with carbon nanotubes, it was decided that UV-VIS spectroscopy should be performed. The control solution was then analyzed. The peaks were saturated in the range of 190-310 nm and no other absorption peaks were observed. The peaks in this range are due to the acetonitrile and aniline and are apparent in all UV-VIS spectra that contain aniline and acetonitrile. The solution with CNT also contained these peaks along with a peak in the 347 nm range, a peak in the 440 nm range and a peak in the 510 nm range. The solutions were very concentrated so it was hard to determine exactly where the products were absorbing.
3.4.2 Influence of Hydrogen Peroxide Concentration

The next step of experimentation included making solutions that contain 1M aniline and 2 M hydrogen peroxide in 25 mL of acetonitrile. One solution contained 100 mg CNT and one control solution without CNT. These solutions were stirred at room temperature for three hours. The solution without CNT became a light yellow color and the solution with CNT became a dark red color at the end of the three hours. The solutions were then analyzed by GC/MS and it was determined that aniline, acetonitrile, carbon dioxide, nitrobenzene and nitrosobenzene were present in both samples; however, the solution with CNT produced both more nitrobenzene and more nitrosobenzene than the solution without CNT when comparing peak areas. Solutions containing 1 M aniline and 3 M hydrogen peroxide were then made in 25 mL acetonitrile, one containing 100 mg of CNT and one without. The solution without CNT again turned a light yellow color at the end of the three hour stirring period. The solution with CNT turned a dark red-
brown color. When analyzing the GC/MS data, it was determined that the 1:3 solution without carbon nanotubes had produced 2.6 times more nitrosobenzene and 5.4 times more nitrobenzene than the 1:2 solution. It was also determined that the 1:3 solution with CNT contained 45.73% azoxybenzene and less nitrosobenzene and nitrobenzene than the solution without CNT. The 1:2 solutions were then analyzed after 24 hrs to determine whether any change had occurred in the samples when exposed to air overnight. The solution containing CNT now had increased nitrobenzene and nitrosobenzene concentrations and also had an azoxybenzene peak that had not been present on the previous day. The solution without CNT also had an increased amount of nitrobenzene; however, the amount of nitrosobenzene present remained the same and azobenzene now appeared in the mass spec.

It was then determined that the solutions containing 1 M aniline and 1 M peroxide that had been refluxed on the first day should be re-analyzed by GC/MS to determine what kinds of changes had occurred. It seemed that the longer the solution was allowed to keep reacting, the greater the number of products present. These solutions that had previously only contained aniline, acetonitrile and carbon dioxide now contained nitrosobenzene, nitrobenzene and azoxybenzene.

3.4.3 Role of Solvent on Oxidation

The next step was to change the solvent used in the experiment. In this case, 1 M aniline, 1 M hydrogen peroxide and acetone were refluxed in a water bath at 60 ºC for 2 h 20 min and then analyzed by GC/MS and UV-VIS. The same solution was then made by adding 100 mg CNT to determine the differences. In this case, three new peaks were
found in the GC/MS data. These correspond to retention times of 14.03 min with a m/z of 207, 14.85 min with a m/z of 133 and 15.39 min with a m/z of 123. The most substantial of these three peaks is the 15.39 min peak with a peak area greater than 20%. The solution without CNT also contained an azoxybenzene peak. The UV-VIS data showed two peaks for the sample without CNT, one at 210 nm and one at 327 nm. The 210 nm peak represents acetone and the 327 nm peak represents nitrobenzene.

![Graph](image)

**Figure 20.** 1:1 Aniline:hydrogen peroxide in acetone reactions.

The CNT solution absorbs in three different regions, at 210 nm, 348 nm and 496 nm. The 210 nm peak also represents acetone, the 348 nm and 496 nm peaks have not yet been determined. They could be azobenzene, azoxybenzene, nitrobenzene or nitrosobenzene. Due to the fact that the solutions are colored after refluxing, it was determined that the peaks are either due to azobenzene or azoxybenzene. cis-
Azobenzene and trans-azobenzene are both orange-red in color and exists as solids. cis-Azoxybenzene is colorless and trans-azoxybenzene is bright yellow in color. Both exist as solids [30a]. The color of the solution is more representative of azobenzene; however, the mechanism of the reaction has not yet been determined. After analyzing the GC/MS data, it was determined that the peaks at 14.05 min and 15.39 min correspond to products formed when aniline and acetone couple with each other. The peak at 14.85 min is nitrobenzene.

3.4.4 Test For Hydrogen Peroxide inside the Nanotubes

To determine whether the hydrogen peroxide was filling up the CNTs, acetone and hydrogen peroxide were refluxed for three hours at 40 °C. Once the reflux was complete, 1 mL of aniline was then added to the reaction flask. The reason for this was to determine whether the peroxide was filling up the nanotubes. If this were the case, the amount of aniline left over in the reaction would be greater with the nanotubes present than without the nanotubes. This, however, was not the case, and the results were consistent with previous results in that the solution containing CNTs produced more nitrobenzene and nitrosobenzene than the solution without CNTs.

3.4.5 Possible Mechanisms

The mechanism of the reaction was then determined. In the control solution, the aniline is initially oxidized to hydroxylamine, then to nitrosobenzene, then to nitrobenzene. The oxidation is due to the excess amount of hydrogen peroxide present in the sample. After long periods of time, the nitrobenzene present in the solution couples
with the excess aniline to form azoxybenzene.

\[ \text{NH}_2 \rightarrow \text{H}_2\text{O}_2 \rightarrow \text{NHOH} \rightarrow \text{NO} \]

\[ \text{O}_2 \]

\[ \text{NO}, \text{azoxybenzene} \]

**Scheme 1.** Outline of reaction mechanism for the control solution.

When acetone is used as the solvent, another side-product is formed which is caused by the coupling of acetone with the aniline to form the following product.

\[ \text{N-(propan-2-ylidene)benzenamine} \]

**Scheme 2.** Side-product formed when aniline and peroxide react in acetone.

This product only occurs when acetone is the solvent. It occurs when the carbonyl group couples with the amine group of the aniline present in the solution.

The reaction that contains carbon nanotubes follows a similar reaction pathway due to the fact that the reaction is still taking place in the outside solution. Again,
hydroxylamine, nitrobenzene and nitrosobenzene are formed and the nitrobenzene couples with excess aniline in the solution to form azoxybenzene. When CNTs are present; however, the solution now has the option of flowing into the nanotubes, being directed in by the functionalized ends. When this occurs, the products that have already been formed are now being held in close proximity to each other. This provides a new product, the coupling of excess aniline with nitrobenzene formed both in the outside solution that has diffused into the nanotubes and nitrobenzene that has already been oxidized inside the nanotube. In this case, azobenzene is formed.

\[
\text{NH}_2^+ + \text{H}_2\text{O}_2 \rightarrow \text{NH}_2\cdot \text{OH} \rightarrow \text{NO} \rightarrow \text{NO}_2
\]

\[
\text{O}_2 \rightarrow \text{azobenzene}
\]

**Scheme 3.** Outline of the carbon nanotube reaction.

This accounts for the product peak seen in the UV-VIS spectrum at 347 and 410 nm. The 347 nm peak represents trans-azobenzene, the \( \pi \rightarrow \pi^* \) transition, and the 410 nm peak, the \( n \rightarrow \pi^* \) transition represents cis-azobenzene. The peak at 510 nm seems to be a
product of nucleophilic aromatic substitution for hydrogen (NASH) which occurs when aniline couples with azobenzene in the presence of functionalized carbon nanotubes. The only time that the 510 nm peak is present is when heat is applied or the solution is kept in the presence of CNTs for long periods of time.

![Figure 21. Azobenzene in acetonitrile reference spectrum.](image)

3.4.6 Catalysis of Carbon Nanotubes

It was then determined that the nanotubes acted as a catalyst for this organic reaction. When nanotubes were present, the amount of nitrosobenzene and nitrobenzene was greater in all cases. The limitations of the carbon nanotube catalysts were not
known, so, the time-dependence of the reaction was determined using UV-VIS analysis. The 347 nm peak was monitored when 1 M aniline and 1 M peroxide were present in acetone with 100 mg CNTs. The absorbance of the solution was measured every 5 min for 1 hour and the results are shown in Figure 22. The peaks at 348 nm and at 510 nm grew with time when CNTs are present. The control solution was also monitored for the 327 nm peak (nitrobenzene), which also grew with time. There were no peaks present at longer wavelengths than 327 nm at any time when monitoring the control reaction.

![Kinetic spectra - CNT in acetone for 1 hour](image)

**Figure 22.** 1:1 Aniline:peroxide monitored every 5 minutes for 1 hour – kinetic method

### 3.4.6.1 Estimation of Azobenzene Concentration

Once the product was identified, the concentration of azobenzene in the solution after the reaction had occurred was determined. Azobenzene was dissolved in acetonitrile at different concentrations to determine the molar extinction coefficient (ε) by UV-VIS analysis. This was determined to be $7.317 \times 10^3$ M$^{-1}$cm$^{-1}$ for trans-azobenzene and 470 M$^{-1}$cm$^{-1}$ for cis-azobenzene. Because the CNTs catalyze the reaction, the
amount of carbon nanotubes present in the solution should have an effect on the amount of azobenzene that is formed. Three different solutions containing 1 M aniline and 1 M hydrogen peroxide were made containing 100 mg, 120 mg and 150 mg of CNTs, respectively. The amount of azobenzene formed was determined by monitoring the peak at 347 nm using Beer’s Law shown below:

\[ A = \varepsilon b c \]  

(Eq. 1)

where A is the absorbance in the UV-VIS region of the spectrum, b is the path length of the cuvette and c is the concentration at the specified wavelength. A, \( \varepsilon \) and b are known which allows us to calculate c, the concentration of azobenzene. Figure 23 shows the Beer’s law plot for various azobenzene concentrations dissolved in acetonitrile. The slope of the line is equal to the molar extinction coefficient at the indicated wavelengths.

![Beer's Law Plot for Cis- (410nm) and Trans-Azobenzene](image)

**Figure 23.** Beer’s Law plot for cis- and trans-azobenzene.

The following graph (Figure 24) shows the concentration of azobenzene with respect to the time and the amount of CNTs present. The three amounts of CNTs that were added
to the solutions are shown. It is obvious from the graph the amount of CNTs affects the amount of azobenzene formed. As the amount of time and the amount of carbon nanotubes are increased, the concentration of the azobenzene in the solution increases. As you can see, the 120 mg and 150 mg curves are practically straight lines from 5 min to 50 min, whereas the 100 mg curve begins to level off at approximately 20 minutes. When large amounts of CNT are present, there are enough nanotubes to continuously produce azobenzene for at least one hour. When less than 120 mg CNT are present, the amount of azobenzene produced seems to stall. This shows that the carbon nanotubes act as a true catalyst with the amount of the catalyst having a direct effect on the reaction.

Figure 24. trans-Azobenzene concentration vs. time for varying amounts of CNT.

3.4.6.2 Azobenzene Diffusion Profiles

When the solution is in the presence of nanotubes, azobenzene is formed. This occurs because the molecules have entered into the nanotubes and are being held within
such a close proximity that they react. The process by which they enter the tubes has been determined to be diffusion-controlled following Fick’s Law of Diffusion (30b) which is described in the following equation:

\[ c_t = c_o \text{ erf} \left( \frac{x}{\sqrt{D}t} \right) \]  

(Eq. 2)

where \( c_o \) represents the concentration of the solution inside the nanotube, \( c_t \) represents the initial concentration of the reactants, \( x \) is the distance between the two media, \( D \) is the diffusion rate constant of the solvent and \( t \) is the length of time it takes for the solution to diffuse into the nanotubes.

![Simulation of Error Function Curve (Fick's Law)](image)

**Figure 25.** Simulation of Fick’s Law error function curve for the diffusion of reactants into the nanotubes and products out of the nanotubes.

The simulation of the diffusion controlled reaction is shown in Figure 25. The concentration of the solution coming out of the tubes compared to the initial concentration of the reactants was monitored and plotted to show that the reaction
follows the error function. The diffusion rate constant of the reactants in acetonitrile is $1 \times 10^{-6}$ cm$^2$/min.

### 3.4.6.3 Supportive Evidence for Reaction inside the Nanotubes

Because the solution diffuses into and out of the nanotubes, it was important to determine what happens to the solution once it enters the nanotubes. To do this, 150 mg of CNT were added to a 1 M aniline and 1 M H$_2$O$_2$ in acetonitrile. After the reaction was allowed to proceed for 1 hr, the excess solution was filtered off and the nanotubes were washed and dried. The nanotubes were then placed in hexane and sonicated for $\frac{1}{2}$ hr to determine whether any product had remained inside the nanotubes. This solution was then analyzed by UV-VIS and the results can be seen in Figure 26. After sonication, the same product peaks could be seen in the hexane solution as in the original solution. A peak at 347 nm was visible

![Solution Remaining in the Nanotubes after Extraction](image)

**Figure 26.** Extraction of the solution inside the nanotubes.
representing azobenzene, one at 230 nm which represents hexane and one at 290 nm which represents acetonitrile. This experiment proved that the solution was entering the nanotubes and that the product formed inside the nanotubes is identical to the original solution.

3.4.6.4 Stereospecificity of Azobenzene

The next step was to determine whether the carbon nanotubes promoted stereospecific azobenzene formation. As can be seen in Figure 21, azobenzene is produced both as trans, the thermodynamic product formed at 347 nm, and cis, the kinetic product formed at 410 nm. trans-Azobenzene is produced in higher quantities in the first twenty minutes of product formation. As the reaction continues, more cis-azobenzene is formed. As calculated from Figure 19, the average for all of the time intervals is approximately twice the amount of trans-azobenzene as cis-azobenzene. According to these values, the product is 80% stereoselective for trans and 20% for cis. To prove that the two peaks in question are azobenzene peaks, a cis/trans isomerization experiment was performed. Here, the UV-VIS spectrum of the product was obtained at ½ hr. The solution remained in the cuvette for ½ hr longer and was exposed to 347 nm light during that time period. This illumination caused an increase in the peak at 410 nm and a decrease in the peak at 347 nm showing that the cis and trans absorbances for azobenzene do occur at these wavelengths. This is further evidence that azobenzene is our product.

3.4.6.5 Oxidation under Inert Atmosphere

The next step was to determine whether the carbon nanotubes were catalyzing the
reaction, or whether it was excess oxygen present in the reaction flask and the nanotubes. 150 mg of CNT were added to a reaction flask along with a 1 M solution of aniline and 1 M hydrogen peroxide in acetonitrile. The flask was fitted with a water-cooled reflux condenser. Nitrogen gas was bubbled through the reaction mixture as it was heated to 40 °C for 1 hour. The products were identified and the quantities produced were compared to the reaction that had no nitrogen bubbling. There were no major differences between the two products when analyzed by either GC/MS or UV-VIS. The results helped to prove that the nanotubes are the sole catalysts of the production of azobenzene when CNT are present in the solution.

3.4.6.6 Formation of NASH Product

Three different methods were used to determine the products of the 1:1 reaction of aniline with peroxide. To begin with, the reactants were placed in a reaction flask fitted with a reflux condenser and heated at different temperatures to determine whether temperature had an effect on the reaction. The amount of products does increase with temperature; however, so does the amount of the NASH product and azoxybenzene produced from the outside reaction that is unwanted. Once it was determined that room temperature gives the most optimum temperature conditions, reactions were performed at room temperature with the carbon nanotubes added at the bottom of a test tube or cuvette. This type of setup, referred to as the kinetic method, gave results that were purely diffusion controlled. When the reaction was done in a cuvette and monitored by UV-VIS in the kinetic mode, the product came out of the nanotubes in streams of orange-red color. The reaction solution was not homogeneous in that the streams were clearly
visible as can be seen in Figure 10. The streams resulted in values in the UV-VIS spectrum that were inconsistent, because they solely depended on the time that it took for the product to move up the cuvette into the path of illumination of the UV-VIS. The advantage to this method is that the carbon nanotubes always settle at the bottom of the vessel and never interfere by scattering UV light. The final method used eliminated the problems with the homogeneity of the solution. The nanotubes and reactants were placed in an Erlenmeyer flask with a magnetic stir bar and stirred for the allotted time. We refer to this as the convection method. The reaction solution was analyzed by UV-VIS and stirred constantly throughout the entire reaction. Because the reaction was placed on a magnetic stirrer, nanotubes were floating in the solution as well causing them to interfere with the absorbance of the light from the UV-VIS. The carbon nanotubes are not soluble in the solution, and they reflect the UV light causing scattering. To overcome this, the reaction solution was taken from the flask, put into a cuvette and allowed to sit until the nanotubes settled to the bottom. Because there were still some nanotubes in this solution, the reaction proceeded, so there were some streams of product coming from the leftover nanotubes causing some inconsistencies in the absorbance of the products.
3.5 Analytical Applications

The reaction of aniline with azobenzene using carbon nanotubes as catalysts has a few different uses. The most obvious use is to prepare azobenzene. Other uses include aniline and peroxide detection in solutions and sensors. The aniline and peroxide detection limits will now be discussed.

Figure 27. 1M aniline and 1M hydrogen peroxide in acetonitrile monitored every 5 minutes for 1 hour – convection method.

The amount of aniline and peroxide in the reaction solution were varied to determine the highest and lowest limits of aniline and peroxide detection. The following
Table gives values for the concentration of azobenzene from 3 mM-1 M aniline and 5 M peroxide in solution using the kinetic method.

<table>
<thead>
<tr>
<th>Solution (Aniline:H₂O₂)</th>
<th>Concentration of Aniline</th>
<th>Corrected Absorbance</th>
<th>Concentration of Azobenzene</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:5</td>
<td>9.14E-04</td>
<td>0.852</td>
<td>1.16E-04</td>
</tr>
<tr>
<td>0.5:5</td>
<td>4.57E-04</td>
<td>0.614</td>
<td>8.41E-05</td>
</tr>
<tr>
<td>0.1:5</td>
<td>9.14E-05</td>
<td>0.226</td>
<td>3.10E-05</td>
</tr>
<tr>
<td>0.01:5</td>
<td>9.14E-06</td>
<td>0.038</td>
<td>5.21E-06</td>
</tr>
<tr>
<td>0.003:5</td>
<td>2.74E-06</td>
<td>0.025</td>
<td>3.42E-06</td>
</tr>
</tbody>
</table>

It is obvious from the table above that 1 M aniline produces the most amount of azobenzene; however, at 3 mM aniline, azobenzene can still be detected by the UV-VIS. The visual limitation is approximately 25 mM aniline with 1 M peroxide. A very slight orange color is evident at these levels. At 3 mM aniline, the orange color cannot be seen; therefore, if a device were to be made that would sense the amount of azobenzene in a sample, it would need to be coupled with a detector. A 10 M aniline and 1 M peroxide solution was made and performed in this way. Azobenzene was produced and detected very quickly. The amount of side products formed during this reaction was very high compared to lower amounts of aniline. The GC/MS results are shown for the aniline.
The column used in the GC/MS that produced these results could not detect azobenzene in the sample. When carbon nanotubes were used as catalysts, however, the amounts of nitrobenzene and nitrosobenzene were greater than when the nanotubes were not present. This was contributed to the catalytic effect of the nanotubes. As the amount of nitrosobenzene increases, so does the amount of azobenzene as nitrosobenzene is needed to couple with the excess aniline to form azobenzene. With the exception of the 2:1 ratio of reactants, nitrosobenzene was produced in greater amounts when the CNTs were present. This reaction did not proceed in the same way as the others. There was less aniline conversion at this ratio than at any other. The ratio of reactants that seems to produce the most azobenzene, according to these results, is the 1:2 ratio of aniline to peroxide. Nitrosobenzene and nitrobenzene are produced in 60% greater yields when CNTs are present. These results show the true catalytic nature of the nanotubes and even though the azobenzene cannot be detected, these results can be coupled with the UV-VIS data to show that azobenzene is actually formed. Table 4 gives more proof of the
catalysis of the CNTs.

<table>
<thead>
<tr>
<th>Ratio of aniline to peroxide</th>
<th>%Area of Nitrosobenzene with 100mg Carbon Nanotubes</th>
<th>%Area of Nitrosobenzene without Carbon Nanotubes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1mM aniline to 1mM peroxide</td>
<td>1.53</td>
<td>1.19</td>
</tr>
<tr>
<td>1mM aniline to 1mM peroxide in acetone</td>
<td>0.67</td>
<td>0.6</td>
</tr>
<tr>
<td>1mM aniline to 2mM peroxide</td>
<td>1.76</td>
<td>1.4</td>
</tr>
<tr>
<td>1mM aniline to 4mM peroxide</td>
<td>2.33</td>
<td>1.73</td>
</tr>
<tr>
<td>2mM aniline to 2mM peroxide</td>
<td>2.52</td>
<td>0.5</td>
</tr>
<tr>
<td>5mM aniline to 5mM peroxide</td>
<td>4.33</td>
<td>1.58</td>
</tr>
</tbody>
</table>

As the reaction proceeds, the nanotubes soak up the solution and it then diffuses out of the tubes. Because of this, at any given time, there are some reactants and products inside the tubes. To determine approximately how much solution has entered into the nanotubes, they were filtered from the reaction solution and weighed. The initial weight was 61.5 mg of functionalized carbon nanotubes. After the reaction had proceeded for 1 hr, the amount of carbon nanotubes remaining was 84 mg. This equates to a 136% increase in the weight of the nanotubes after the reaction. This shows that there is a considerable amount of solution remaining inside the nanotubes, so the product yield is
actually much higher than what can be measured.

3.6 Experiments with RPI Carbon Nanotubes

The multiwalled nanotubes from RPI were functionalized to determine whether they would also catalyze the reaction. The functionalized carbon nanotube samples were compared to active carbon and graphite in a honeycomb structure. In theory, the active carbon and the honeycomb graphite should not produce any azobenzene. This would give additional support to show that all functionalized nanotubes effectively bring about the reaction. The honeycomb structure graphite was considered to be a sheet of graphite with tiny holes in a honeycomb shape and was used to determine whether the pores were small enough to promote the close proximity of the reactants to each other. This honeycomb graphite was used as received from Prof. D.D.L. Chung of University of Buffalo and not functionalized in any way. The active carbon, the RPI nanotubes and the DEAL nanotubes were functionalized and used in the reactions in both the functionalized and nonfunctionalized forms.

To begin with, the active carbon and the honeycomb structure were analyzed. Neither the active carbon nor the honeycomb structure produced any azobenzene, whether they were functionalized or not. The honeycomb structure, not being functionalized, may have worked if this had been done. The solution is pulled into the nanotubes not only by diffusion, but by the electron densities that have been previously discussed. The electron densities are not only caused by steps or kinks in the nanotubes, but also by the breaks in the nanotube caused by the functionalization and purification in nitric acid. If the honeycomb structure had been functionalized, it may have generated
these electron densities allowing the reactants to flow inside the holes of the structure more readily and holding the aniline in these sites until it reacted with the nitrosobenzene.

The RPI and DEAL nanotubes were then compared. The RPI sample as such does not act as a catalyst much in the same way as the DEAL nanotubes. Hence, the nanotubes were functionalized according to the procedures discussed earlier. The following table gives the absorbance values at 347 nm of the solutions that contained functionalized RPI and DEAL tubes as catalysts.

<table>
<thead>
<tr>
<th>Time</th>
<th>Absorbance(^\text{a}) DEAL tubes</th>
<th>Absorbance(^\text{a}) RPI tubes</th>
<th>RPI/DEAL</th>
<th>% Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>15</td>
<td>0.48</td>
<td>1.306</td>
<td>0.356</td>
<td>0.644</td>
</tr>
<tr>
<td>30</td>
<td>0.743</td>
<td>1.451</td>
<td>0.512</td>
<td>0.488</td>
</tr>
<tr>
<td>45</td>
<td>0.99</td>
<td>1.581</td>
<td>0.626</td>
<td>0.374</td>
</tr>
<tr>
<td>60</td>
<td>1.186</td>
<td>1.79</td>
<td>0.663</td>
<td>0.337</td>
</tr>
</tbody>
</table>

\(^\text{a}\) All absorbances were measured at 347 nm.

It is obvious from these results that the functionalized RPI tubes are much better catalysts than the DEAL nanotubes. We determined that the functionalized RPI sample contained approximately 50% more nanotubes than the functionalized DEAL sample, which is approximately 30% as quoted from the company. Reactions containing nonfunctionalized nanotubes did not produce any azobenzene peak within the first hour. Even though the RPI nanotubes give a much higher yield of azobenzene, these were not used for the rest of the experimentation because they cannot be obtained commercially.
3.7 Effect of Silica and Light

The reaction was also analyzed in three different types of bottles to determine whether silica or light was a factor in the production of azobenzene. The reactants were placed in a plastic vial, a clear glass vial and an amber bottle and analyzed after 1 hr. The percentage of nitrosobenzene and all other products was equivalent for all three vessels indicating that neither light nor silica has an effect on the reaction.

3.8 Degradation of Carbon Nanotubes

In order to gain more proof that no amount of product was coming from the reactants, solvents or nanotubes by themselves, all of the following were analyzed by both GC/MS and UV-VIS for any detectable product: CNTs in acetone and acetonitrile, aniline in acetone and acetonitrile, CNTs plus aniline or peroxide in acetonitrile and acetone, and hydrogen peroxide in acetone and acetonitrile. For each of these experiments, only peaks and fragments characteristic of those materials were evident and no nitrobenzene, azobenzene, nitrosobenzene or azoxybenzene were detected.

It was not known whether leaving the nanotubes in the presence of CNTs for long periods of time may lead to the breakdown of the CNTs, so, an experiment was designed to determine whether this occurs.
60mg CNTs were placed in acetonitrile and analyzed by GC/MS at approximately ½ hr intervals to 90 minutes. The nanotubes are not left in the reaction solution for longer than 90 min, so if any breakdown were to occur, it should have occurred by this time. In specific, the carbon dioxide peak should increase if the tubes are being broken down. This would be caused by the oxidation of carbon from the ends of the nanotubes. Figure 26 gives the results of this experimentation. A general decrease in the amount of CO₂ (g) is detected by the mass spec indicating that the nanotubes are not broken down within this time frame.

3.9 Oxidation of p-Toluidine

The purpose of this experimentation was to determine whether the oxidation of a
substituted aniline system would be catalyzed by CNTs. The products were identified by GC/MS and UV-VIS and the mechanisms will be shown for both the reaction with nanotubes and without nanotubes. Initial experiments involved a solution of 1 M \( p \)-toluidine and 1 M hydrogen peroxide in acetonitrile. Both the control solution and the solution with 100 mg functionalized carbon nanotubes were allowed to react for 1 hr before analyzing the samples. With these reactions, the volume was held constant at 12-mL to minimize the amount of reactants and solvent used. Initially, there is no product peak in the 400-500 nm range. As the solution is monitored with time, a peak begins to grow at 450 nm.

Using the kinetic method described previously, \( p \)-toluidine reacts with hydrogen peroxide in the nanotubes and produces a color, in this case yellow-orange, that diffuses from the nanotubes to the top of the reaction vessel in an inhomogeneous fashion. Figure 29 simulates this reaction.

![Figure 29](image)

**Figure 29.** Simulation of \( p \)-toluidine reaction.

The red arrows indicate the solution outside of the nanotubes. The blue arrow indicates
the reaction that occurs inside the nanotubes at the bottom of the cuvette. The outside reaction proceeds differently than the reaction that occurs inside the nanotubes. Inside the nanotubes, the reactants are held within close proximity of each other and can react with each other where they cannot do so in the outside reaction. The following figures outline the mechanism of the reaction. This reaction proceeds much in the same manner as the aniline reaction. In the control solution, the amine group is oxidized to hydroxylamine by hydrogen peroxide, and then oxidized to nitrosobenzene and then nitrobenzene. These two steps are caused by the excess hydrogen peroxide in the reaction solution. The nitrobenzene is formed in rather high yields and can couple with excess p-toluidine in the solution to form \( p,p' \)-dimethylazoxybenzene. The reaction containing carbon nanotubes proceeds in the same manner as the control, except for the restriction of the reactants and products inside the nanotubes. When analyzing the solution by GC/MS, nitrobenzene, nitrosobenzene and \( p,p' \)-dimethylazoxybenzene (azotoluene) are present as is \( p,p' \)-dimethylazobenzene (azoxytoluene). The azo product is formed when the \( p \)-toluidine is oxidized to nitrobenzene and couples with the excess \( p \)-toluidine inside the nanotubes.
Scheme 4. Reaction mechanism for \( p \)-toluidine in hydrogen peroxide control solution.

As with the aniline system, when \( p \)-toluidine is reacted with \( H_2O_2 \) in acetone, the \( p \)-toluidine couples with the acetone to form the following side product.

Scheme 5. Side-product of \( p \)-toluidine reacting in acetone.
Scheme 6. Mechanism of \( p \)-toluidine reaction in the presence of FMWCNT.

3.9.1 Spectral and Kinetic Features

The reactions were monitored by UV-VIS for their absorption properties (Figure 30). The control solution showed no peaks that were characteristic of the azo product in the range of 800-290 nm using the convection method described in the previous section.
Figure 30. $p$-Toluidine with hydrogen peroxide control solution (0-135 min).

It is obvious from the above graph that the control solution does not produce any azotoluene. The very first line at the top of the graph was taken at 0 min when the nanotubes had not completely settled in the cuvette, therefore the nanotubes are absorbing light in this region and not the solution. The spectra from 15-135 min, taken at 15 min intervals, starts at the very bottom and goes toward the top as time increases.

The peaks that should occur for $p,p'$-dimethylazobenzene can be seen in Figure 30. This was also done using the convection method.
Absorption spectra of p-toluidine reaction with CNT

![Absorption spectra of p-toluidine reaction with CNT](image)

**Figure 31.** Time-dependent absorbance of p-toluidine reaction with CNT.

It is obvious from Figure 31 that the peak at 447 nm grows with time from 0 min to 135 min. This peak represents azotoluene. This reaction took place in a 25 mL Erlenmeyer flask with 100 mg functionalized carbon nanotubes and a magnetic stir bar. A 0.8 M p-toluidine in acetonitrile solution was made and to this was added hydrogen peroxide to make a 0.8 M solution. The reaction was kept constantly stirring during this part of the experiment and 3 mL of solution were taken from the cuvette and analyzed by UV-VIS in 15 min intervals. Once the removed solution was analyzed, it was placed back into the flask and the reaction was allowed to proceed. Unlike the aniline reaction, there are not two peaks present that represent cis and trans stereochemistry. There is also an unexplained gap between the spectra from 75-90 min and the peak at 120 min seems to be much lower than the 75 min peak. This is not the case. Unfortunately, because the nanotubes are floating in the solution in the convection method, they do not settle at the bottom of the cuvette right away. When looking at the baseline for each of the spectra, it
is easy to see that if all of the lines were corrected to zero, the absorbance of the 447 nm peak would be linear and so would the concentration growth of \( p,p\'-\text{dimethylazobenzene} \). The above data has been graphed in order to show this. The concentration of azotoluene was determined using a molar extinction coefficient of 562 \( \text{M}^{-1}\text{cm}^{-1} \) as found in reference [31]. The extinction coefficient of \( p\)-toluidine was found to be \( 2.3 \times 10^3 \text{M}^{-1}\text{cm}^{-1} \).

![P-Toludine-H2O2-CNT](image)

**Figure 32.** Linearity of the growth of \( p,p\'-\text{dimethylazobenzene} \) with time.

The GC/MS results help to prove the theoretical mechanism. The following graph shows the results of this analysis. This bar graph shows the % area of the \( p,p\'-\text{dimethylazobenzene} \) and \( p,p\'-\text{dimethylazoxybenzene} \) peaks determined by GC/MS. The y-axis is not the actual percentage of azo or azoxy compound formed, only percentage of the total products found in the analysis, including \( p\)-toluidine. As can be seen, the amount of \( p,p\'-\text{dimethylazoxybenzene} \) formed is 4.1% in the control solution and only
1.25% in the solution containing nanotubes. There is no azotoluene peak in the control solution and there is approximately 0.9% in the solution containing carbon nanotubes.

Figure 33. Comparison of GC/MS results of 1:1 p-toluidine reaction with hydrogen peroxide.

The values for azotoluene and azoxytoluene compound formed in the solution that contains carbon nanotubes should be the same amount as the azoxytoluene compound formed in the control solution. The problem is that not all of the p-toluidine is converted; furthermore, the same amount of p-toluidine is not converted in each of the reactions. The reaction without carbon nanotubes is slower than the reaction that contains CNTs; however, some of the solution is trapped inside the CNTs causing the amount of product detected to be lower than the actual amount. In any case, the azotoluene formed comes from the restriction of the nanotubes and the azoxytoluene comes from the outside
reaction.

No reference spectra could be found for azotoluene and the chemical could not be purchased. To determine whether the product formed in this reaction is azotoluene, 0.1 g p-toluidine was dissolved in enough hexane to dissolve the p-toluidine, and then KMnO₄ in solution was added to this. The reaction was left at room temperature overnight. This should result in the oxidation of the p-toluidine to azotoluene.

![Graph](image)

**Figure 34.** *p'*p'-Dimethylazobenzene reference spectra.

Figure 34 shows the UV-VIS analysis of the products formed in this reaction. The azotoluene peak is present in this sample as well at 450 nm. The color is slightly darker than the yellow-orange of the product that is formed when the CNTs are present in the *p-*
toluidine and hydrogen peroxide reaction. The concentration of this could not be determined; however, so the molar extinction coefficient could not be determined by this method.

Considering that the convection method and kinetic method produce different amounts of products, the difference between the two methods was studied. The results of this analysis are shown in Table 6. In this table, the % area of the products was divided by the %p-toluidine conversion to determine the percentage of the specific product in the sample. All measurements were taken using 1 μL of sample in the GC/MS. The listing "others" represents products that could not be determined, NASH products or any polymerization that may occur.

Table 6. Comparison of Kinetic vs. Convection Method for p-Toluidine Reaction.

<table>
<thead>
<tr>
<th></th>
<th>Kinetic no CNT</th>
<th>Kinetic with CNT</th>
<th>Convection no CNT</th>
<th>Convection with CNT</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>%area</td>
<td>%p-toluidine conversion</td>
<td>%products</td>
<td>%area</td>
</tr>
<tr>
<td>p-toluidine</td>
<td>24.92</td>
<td>75.08</td>
<td></td>
<td>p-toluidine</td>
</tr>
<tr>
<td>p-nitrosotoluene</td>
<td>7.15</td>
<td>9.52</td>
<td></td>
<td>p-nitrosotoluene</td>
</tr>
<tr>
<td>p-nitrotoluene</td>
<td>4.47</td>
<td>5.95</td>
<td></td>
<td>p-nitrotoluene</td>
</tr>
<tr>
<td>azoxytoluene</td>
<td>47.34</td>
<td>63.1</td>
<td></td>
<td>azoxytoluene</td>
</tr>
<tr>
<td>others</td>
<td>16.12</td>
<td>21.5</td>
<td></td>
<td>azotoluene</td>
</tr>
</tbody>
</table>

|                  |        |                  |          |           |          |                  |          |
| p-toluidine     | 67.86 | 32.14            |          | p-toluidine | 47.05 | 52.95            |          |
| p-nitrosotoluene| 10    | 31.1             |          | p-nitrosotoluene | 7.68 | 14.5             |          |
| p-nitrotoluene  | 3.18  | 9.89             |          | p-nitrotoluene | 2.95  | 5.57             |          |
| azoxytoluene    | 8.51  | 2.65             |          | azoxytoluene  | 2.32  | 4.38             |          |
| azotoluene      | 2.68  | 8.34             |          | azotoluene    | 6.26  | 11.8             |          |
| others           | 7.78  | 24.2             |          | others        | 10.83 | 20.4             |          |
As was discussed before, the amount of \( p \)-toluidine converted is different for each reaction. After 1hr, the kinetic control reaction has converted the most amount of \( p \)-toluidine. In this case, no azotoluene was present. The amount of azoxytoluene produced by this method is 63.1% of the total of the products. This is also the same amount of azoxybenzene produced by the solution that contains CNTs. The amount of azotoluene formed in by the reaction containing nanotubes is 4.66% as compared to 0% in the control. The amount of nitrosotoluene has also increased in the kinetic reaction with CNTs. This gives further support to the reaction mechanism that has been proposed. The CNTs do not increase the amount of azoxytoluene formed as it is produced solely in the outside reaction. The amount of nitrosotoluene is also increased when CNTs are present showing that this oxidation step is also catalyzed by the nanotubes and occurs within the nanotubes. The nitrosotoluene formed that does not get to couple with the \( p \)-toluidine then diffuses out of the nanotubes into the reaction solution where it can be detected. The amount of nitrotoluene is fairly consistent between the two reactions: 5.95% in the control and 4.28% in the reaction with CNTs.

The convection method results seem to be fairly inconsistent when comparing to the kinetic results. The conversion of \( p \)-toluidine is the opposite in the convection reactions as in the kinetic reactions. More \( p \)-toluidine was converted when CNTs were present in the solution. When the convection method is used, the solution is constantly being stirred allowing the solution to possibly flow into and out of the nanotubes faster than the kinetic reaction will allow. The convection method increases the diffusion of the solution into and out of the nanotubes. Keeping this in mind, the amount of azotoluene is greater in the convection reaction with CNTs than in the kinetic reaction with CNTs by
approximately 40%. However, unlike the kinetic control reaction, the convection control reaction contains 8.34% azotoluene. The convection reaction with CNTs also contains 60% more azoxytoluene than the control reaction. The convection reaction also contains more nitrosotoluene in the control than when CNTs are present. With the exception of the azoxytoluene, all of the products occur in greater amounts when the convection method is used.

The main difference between the kinetic and convection methods is that the convection method is constantly being stirred. The solution and nanotubes, if they are present, are constantly in motion causing a slight increase in the temperature of the reaction thereby increasing the reaction. The temperature of the reaction was not monitored. As the temperature increases, the molecules begin to move faster, increasing the chances of colliding with one another and forming products. Both the control and the CNT reaction were performed on a hotplate equipped with a magnet for stirring the stirbar. They were placed on the hot plate at the same time. If the major difference between the two methods is stirring, it is important to keep the solutions stirring constantly at the same speed. If they are not, the rate at which the reaction occurs will be different as is the case here. The amount of p-toluidine should be similar when CNTs are present and when they are not if the reaction were to be rate-controlled. In this case, the convection control reaction has converted approximately 60% of the p-toluidine that was converted in the reaction that contains nanotubes. When comparing the amount of azoxytoluene in the two solutions, it can be noted that the amount formed in the control is also 60% of the amount formed in the reaction containing CNTs. Therefore, the amount of azoxytoluene formed in each case is essentially the same. As for the amount of
nitrosobenzene, the convection control reaction produces approximately 33% more than the CNT reaction when taking into account that nitrosotoluene is needed for azotoluene production. More nitrotoluene is also formed in the control solution as it should be.

Once the differences between these two processes were determined, a kinetic study was done on the kinetic reactions.

![p-Toludine-H2O2-CNT](image)

**Figure 35.** Kinetic study of 1:1 p-toluidine to hydrogen peroxide reaction.

By plotting the log of the concentration vs. the time for the 1:1 reaction of p-toluidine with hydrogen peroxide, it was determined that the reaction follows a pseudo-first order mechanism where the slope of the line, the rate constant, is $0.0093 \text{ s}^{-1}$ Scheme 7 shows the pathway of the kinetic mechanism. It assumes the path of $p$-toluidine directly converting to azotoluene as the product.
Scheme 7. Kinetic mechanism of the p-toluidine reaction.

3.10 Oxidation of Methylamine

The methylamine used in these experiments was purchased from Aldrich as a solution (41% in water) and could not be purified. Initial results showed that the 1 mM methylamine reaction with 1 mM peroxide was rather violent both when functionalized nanotubes were present and in the control solution. The solutions bubbled and turned very warm when acetonitrile was the solvent. When acetone was the solvent used, the solution bubbled and produced a small amount of heat for about half a minute and then was calmer. Based on earlier discussions, the expected product is the colorless azomethane gas. As expected the reaction did not result in a colored product, therefore no UV-VIS spectrum could be obtained. GC/MS analysis showed $m_z=58$ which may represent the formation of azomethane; however, acetone also has the same mass number which precludes any assignment.

4. Concept of Nanosynthetic Machine

4.1 Principle

Once the mechanism of the reaction was established after analyzing the products by UV-VIS absorption spectroscopy and GC/MS, it was obvious that the outside reaction
had too much influence on the amount and kinds of products that were detected. A nanosynthetic machine concept was brought about to eliminate the amount of azoxybenzene, nitrobenzene and nitrosobenzene products that were detected mainly when the CNTs were not present. The idea, then, is to eliminate the outside reaction by allowing the solution to flow only through the nanotubes. Hopefully, this will eliminate the undesired products and produce a sole product that is unique to this system, namely, a substituted azobenzene.

### 4.1.1 Proposed Construction

In order to completely eliminate the outside reaction, a device must be developed that contains the CNTs on a substrate in a manner that will allow the solution to only flow through them. The proposed construction can be seen in Figure 36.

![Diagram of Proposed Construction](image)

**Figure 36.** Proposed construction of nanosynthetic machine.
The nanosynthetic machine consists of a reaction inlet, a nanopump, a reaction outlet and a detector coupled to the machine. The reaction inlet is the part of the nanomachine where the initial reactants in solution will be placed. The nanopump may or may not be needed in the design. The solution will flow from the inlet through the functionalized nanotubes to the reaction outlet where the product or products can be detected, analyzed and collected. The nanopump may be needed for two reasons. First of all, the solution may not flow through the nanotubes on its own. Here, the nanopump would be helpful in aiding the solution through the nanotubes. The nanopump may also be needed to recycle the solution back through the nanotubes in the case that either the reactants are still present in the product or 100% of the product is not produced and the solution needs to be directed back through the tubes in order to make this happen.

4.2 Preliminary Attempts and Results

4.2.1 Simulation of a Nanosynthetic Machine.

The nanosynthetic machine was simulated by forming a column of carbon nanotubes inside either a micropipette tip or a Pasteur pipette tip. The pipettes were filled with functionalized MWCNT and lightly packed to allow the CNTs to stay within the pipette tip and not come out with the product. The length of the smallest micropipette tip is 3.2 cm. This was the column used most often. Two larger micropipette tips were used that had lengths of 3.35 cm and 5.1 cm. The diameter of the two smallest micropipette tips is 0.5 cm where the largest micropipette tip has a diameter of 0.75 cm. The length of the Pasteur pipette tip was also 5.5 cm however it has a much smaller diameter than the
micropipette tips at approximately 0.1 cm.

Table 7. Measurements for Carbon Nanotube Columns.

<table>
<thead>
<tr>
<th></th>
<th>Micropipet Tip</th>
<th>Pasteur Pipet</th>
</tr>
</thead>
<tbody>
<tr>
<td>length (cm)</td>
<td>3.2 3.35 5.1</td>
<td>5.5</td>
</tr>
<tr>
<td>diameter (top-cm)</td>
<td>0.4 0.4 0.75</td>
<td>0.1</td>
</tr>
<tr>
<td>diameter (bottom-cm)</td>
<td>0.05 0.05 0.1</td>
<td>----</td>
</tr>
<tr>
<td>Volume (cm³)</td>
<td>0.15 0.16 0.86</td>
<td>0.043</td>
</tr>
</tbody>
</table>

Table 7 shows the parameters for the nanotube column. Each column can be packed with 90-100 mg CNTs with the exception of the large micropipette tip which can hold 150 mg or greater.

The aniline or peroxide solution was then made and added dropwise to the column and allowed to flow through by gravity. The solution is soaked up by the carbon nanotubes and the product then flows out by diffusion where it can be collected. The micropipette tips were the loosest packed which provided the easiest pathway for the solution to flow through the column. This can be seen when comparing the volume of the tips to the amount of CNTs that are entered into them. The 3.2 cm column has a volume of 0.15 cm³ whereas the Pasteur pipette tip has a volume of 0.043 cm³. Each of these can hold the same amount of CNTs in their column therefore the Pasteur pipette tip must be much more tightly packed. This happened to be the case when each of the columns was tested. The small tip can hold approximately 0.75 mL of solution above the nanotubes. The Pasteur pipette tip can hold much more because it is taller; however, when the same amount of solution was placed in both, the solution traveled through the
micropipette tip at a rate that is more than two times as a fast as it flowed through the Pasteur pipette. The carbon nanotubes were just too densely packed into the Pasteur pipette tip to be a logical choice for future nanomachine simulations.

Sometimes the carbon nanotubes are bundled together. Even after a small amount of grinding with a mortar and pestle, the nanotubes can still bundle together. One of the problems with this bundling is that when a solution is entered into the nanotube column, the nanotubes get packed down. As they are packed down, the nanotubes that are bundled together get caught inside the micropipette tip or Pasteur pipette causing the solution to stop flowing through the column. This problem was more prevalent when the Pasteur pipette was used, thus another reason that the micropipette tip was chosen as the main support for the column.

The nanosynthetic machine simulation is not a perfect system; however, it provides the information necessary to go on with plans to build the nanomachine. The simulation provides enough proof that the expected results will occur when the solution is allowed to travel through the nanotubes solely. The nanotube column still allows the solution to flow around the outside of the nanotubes; however, it is a very small amount. This method was used to determine the products for four different amine starting materials: aniline, p-toluidine, methylamine and diphenylamine. The results of the simulation are shown in the next sections.

4.2.2 Aniline Oxidation Reaction.

Initially, a micropipette tip was filled with 100 mg functionalized multiwalled carbon nanotubes and tapped on the bench top to slightly pack down the CNTs. In a 25-
mL vial, 1 mL of aniline, 1.1 mL of hydrogen peroxide and enough acetonitrile to make a total solution of 12 mL. Five drops of the solution, approximately 0.25 mL, was added at the top of the nanotube column which was held upright (vertical). The solution was then allowed to flow through the column by gravity. Three drops of product were collected on a quartz microscope slide and analyzed by UV-VIS. The three drops were absorbed by the CNTs and after 5 minutes, two more drops were added to the column. After three minutes, one drop was collected on the slide that was completely clear. Three minutes later, three more drops were added which resulted in the collection of a deep red colored product. Another slide was placed on top of the slide that the drops had been collected on, and the sample was analyzed by UV-Vis.

![Figure 37](image)

Figure 37. Product of aniline reaction from simulated nanomachine – first collection.
The results of the UV-VIS analysis are shown in Figure 37. The spectrum is not very different from that of the previous reactions when the CNTs are lying in the bottom of the reaction vessel. There is a large peak at 347 nm and a small peak at 510 nm. This was just a preliminary attempt to determine whether the CNT column was successful and was not analyzed by GC/MS.

The second attempt at making a nanomachine was also done using the smallest micropipette tip. The times for each collection and other specifications can be seen in Table 8. After adding 0.5 mL to the top of the column, the first drop was collected within the first twenty seconds. As before, this drop was almost colorless, with the slight yellow tint of the starting solution, the 1:1 aniline:peroxide solution in acetonitrile. The second drop was collected at 1 min and it was a medium-red color indicative of azobenzene.

<table>
<thead>
<tr>
<th>Specification</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume of micropipet tip</td>
<td>0.15 cm³</td>
</tr>
<tr>
<td>Weight of nanotubes</td>
<td>0.097 g</td>
</tr>
<tr>
<td>1st addition of 0.5mL</td>
<td></td>
</tr>
<tr>
<td>Time for first drop</td>
<td>19 s</td>
</tr>
<tr>
<td>Time for first colored drop</td>
<td>60 s</td>
</tr>
<tr>
<td>Time for all of solution to drop</td>
<td>4 min 42 s</td>
</tr>
<tr>
<td>2nd addition 0.5mL</td>
<td></td>
</tr>
<tr>
<td>Time for first drop</td>
<td>15 s</td>
</tr>
<tr>
<td>Total time of collection</td>
<td>5 min 11 s</td>
</tr>
<tr>
<td>3rd addition of 0.5mL</td>
<td></td>
</tr>
<tr>
<td>Time for first drop</td>
<td>15 s</td>
</tr>
<tr>
<td>Total time of collection</td>
<td>5 min 44 s</td>
</tr>
<tr>
<td>4th addition of 0.5mL</td>
<td></td>
</tr>
<tr>
<td>Time for first drop</td>
<td>15 s</td>
</tr>
<tr>
<td>Total time of collection</td>
<td>6 min 9 s</td>
</tr>
</tbody>
</table>

Table 8. Specifications for Aniline Reaction
It was clear that the solution that was collected after the first 0.5 mL was not 100% product, rather a mixture of the product coming out of the nanotubes and the starting material. Because of this, a second 5 mL aliquot was added to the column to determine what the product would look like at a longer time period. Another 0.5 mL was then added to the column. After approximately 15 sec, the first drop was collected. This time the drop was very dark red in color. When the reaction had been done previously, the nanotubes were placed in the bottom of a reaction vessel and the reaction solution remained above this. The product that diffused out of the nanotubes had always been dispersed in the solution, so, the color of the product could never exactly be determined. It was surprising when it was as deep red in color as it was. As more solution was added to the nanotube column, the color never became deeper and the amount of time necessary for 0.5 mL to flow through the tube was pretty constant at ~5 min.

These collections were then analyzed the next day by GC/MS. The major results can be seen in Table 9. Some products were left out because they were either in very low yield or their identity could not be determined. Because the solution is in the presence of excess hydrogen peroxide and aniline, even after it has been run through the CNT column, the aniline continues to get oxidized by the hydrogen peroxide. There also may be a small amount of nanotubes that have been collected with the product. This accounts for the numerous products detected by the GC/MS after 24 hours.
Table 9. GC/MS Analysis 22h after Collecting from Nanomachine

<table>
<thead>
<tr>
<th>Collection 1</th>
<th>Retention time (min)</th>
<th>Peak Area (%)</th>
<th>Mass Number</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.33</td>
<td>5.32</td>
<td>28, 53, 80, 109</td>
<td>hydroxylamine</td>
<td></td>
</tr>
<tr>
<td>3.71</td>
<td>10.39</td>
<td>66, 93, 121</td>
<td>nitrobenzene</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>28, 51, 77, 105, 152, 182</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.64</td>
<td>16.86</td>
<td>51, 65, 77, 91, 105, 182</td>
<td>azobenzene</td>
<td></td>
</tr>
<tr>
<td>6.81</td>
<td>29.27</td>
<td>141, 169, 198</td>
<td>azoxybenzene</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Collection 2</th>
<th>Retention time (min)</th>
<th>Peak Area (%)</th>
<th>Mass Numbers</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.35</td>
<td>2.05</td>
<td>28, 53, 80, 109</td>
<td>hydroxylamine</td>
<td></td>
</tr>
<tr>
<td>3.73</td>
<td>2.64</td>
<td>28, 39, 66, 93, 121</td>
<td>nitrobenzene</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>28, 77, 93, 105, 152, 182</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.66</td>
<td>3.51</td>
<td>51, 65, 77, 91, 105, 182</td>
<td>azobenzene</td>
<td></td>
</tr>
<tr>
<td>6.83</td>
<td>14.65</td>
<td>141, 169, 198</td>
<td>azoxybenzene</td>
<td></td>
</tr>
<tr>
<td>17.75</td>
<td>60.28</td>
<td>77, 260, 272, 288, 77</td>
<td>NASH product</td>
<td></td>
</tr>
</tbody>
</table>

Table 9 shows all of the products that were detected by the GC/MS using an SPB5-5% phenyl 95% polysiloxane capillary column with the measurements of 15.0 m x 200 μm x 0.20 μm nominal. The flow rate for this column is 2.2 mL/min. The following parameters were taken from [32]: injection temperature = 280 °C, He gas flow rate of 1 mL/min, 1 min at 80°C, increase from 80-220 °C at 20 °C/min and increase from 220-280 °C at 4 °C/min. What is interesting from these results is that the major product from early tests was nitrosobenzene. There is no nitrosobenzene present in these products. The azoxybenzene, which is present in higher yields than azobenzene after almost 24 h comes from the coupling of aniline and nitrobenzene that is formed from the excess aniline and peroxide left in the collection. This is the first time that hydroxylamine was found in any of the results, showing that this step indeed does take place. This could only be theoretically proven in the previous analysis. The second collection also shows 60% of the total product is what we call NASH product. In this case, it is the coupling of 75
azoxybenzene with excess aniline in the solution.

The first nanotube column was then taken approximately one week later and another 1:1 aniline:peroxide solution was added to the column. The first drop was collected at 35 sec and the total in 6 min 8 sec. This is important when comparing these times to the times in table 8. By this time, the solvent should have completely dried from the column and from the nanotubes. The fact that the time for the first drop to be collected was almost twice as long as a column that had not been previously used indicates that the nanotubes have been filled with solution. This first collection was a deep-red color as it had been when the last drop had been collected. It also suggests that the best pathway for the solution to travel through the column is in the nanotubes. Because the first collection here was colored, it may also suggest that some of the product had been adsorbed by the nanotubes. When the solution was placed in the column and began to flow through, the azobenzene and other products, if any, dissolved in the acetonitrile. The product(s) inside the nanotubes were also dissolved in the solution or pushed out of the nanotubes by the solution. This is similar to the reaction that had previously been done to show that the reaction had occurred inside the nanotubes by sonicating the nanotubes in hexane and analyzing by UV-VIS absorption spectroscopy.

To determine exactly what product is formed at each collection, a new column was made with the same measurements as the previous columns. Again, a 1:1 solution of aniline to peroxide was made and 0.5 mL was added to the column. Immediately after the 0.5 mL of solution was collected, it was analyzed by GC/MS for the products. The first collection contained two product peaks, one at a retention time of 3.72 min representing nitrobenzene and one at a retention time of 5.65 min representing
azobenzene. The azobenzene peak was approximately 80% of the total products and the nitrobenzene peak approximately 20%. The second and third collections yielded three major peaks: the nitrobenzene peak at a retention time of 3.7 min, the azobenzene peak at 5.65 min and the NASH product at 17.72 min. The third collection also had produced a small amount of azoxybenzene. In all of the collections, the largest peak was the azobenzene peak. However, the NASH product peak grew the fastest as the azobenzene peak remained approximately the same in all of the collections. It then became apparent that maybe the 1:1 aniline to peroxide solution was not the ideal system and that less aniline should be added in order to inhibit the formation of the NASH product.

At this point, three different ratios of aniline to peroxide were compared: the 1:1 solution reported above, a 1:2 solution and a 1:3 solution. In each case, three 0.5 mL collections were run through the CNT column and analyzed by GC/MS. The 1:2 solution yielded slightly different results. The first collection, analyzed immediately after collection, contained many more product peaks than the 1:1 collections. There were three major peaks, the nitrobenzene peak with a peak area of 12.07%, the azobenzene peak with a peak area of 24.97% and the azoxybenzene peak with a peak area of 29.10%. All other peaks were less than 4.5% of the total products. There was also a very small amount of hydroxylamine formed (2.77%) The total abundance for each of the peaks was less than 230,000. The 2\textsuperscript{nd} collection yielded a smaller number of products which was caused by the increase in abundance of the products formed. Again, there were four major product peaks, the hydroxylamine (retention time of 3.36 min) with a peak area of 4.3%, nitrobenzene with a peak area of 11.82%, azobenzene with a peak area of 23.82%, and azoxybenzene with a peak area of 29.73%. In this case, the relative abundance was
approximately 300,000 or less for each of the products. The larger the relative abundance of these peaks, the smaller the insignificant peaks will become insomuch as they will not be detected by the MS. Some of the smaller peaks may even come from the GC column.

The third collection was very similar to the third collection from the 1:1 sample. Hydroxylamine, nitrobenzene, azobenzene and azoxybenzene peaks are all present with peak areas of 2.12%, 9.28%, 13.21% and 11.62%, respectively. This time, a fifth peak was present in a very large quantity at a retention time of 17.60 min indicative of the NASH product. Here, the relative abundances of each of the peaks is 1.7x10^6 or less which is considerably greater than with collection 2. For each of the collections, a 1 μL sample is injected into the GC. If this varies, the relative abundances will be increased or decreased depending on the discrepancy. However, in all cases, the relative abundance was greatest for the azobenzene peak.

The first collection of the 1:3 solution provided a much cleaner spectrum, largely due to the increased concentration of the products formed. The hydroxylamine peak has an area of 8.18%, nitrobenzene has 9.85%, azobenzene has 16.32% and azoxybenzene has 61.81%. The relative abundance of the azoxybenzene peak is 5.2 x 10^6 and the others are less. The second collection yielded rather large amounts of many different products. The largest peaks are hydroxylamine with a peak area of 3.56%, nitrobenzene with a peak area of 8.48%, azobenzene with a peak area of 11.32% and azoxybenzene with the largest abundance and peak area (52.4%). The main peaks of the third collection are hydroxylamine with a peak area of 7.03%, nitrobenzene with a peak area of 9.58%, azobenzene with a peak area of 16.03% and a large amount of azoxybenzene (45.4%). A small amount of the NASH product is present, only 2.65%. The relative abundance of all
the peaks is basically the same in all three collections.

When comparing the first collection of the three different solutions, it seems that the larger the amount of hydrogen peroxide, the larger the amount of azoxybenzene formed. This is due to the fact that the excess hydrogen peroxide allows the nitrosobenzene to be oxidized to nitrobenzene before coupling with the aniline. This indicates that possibly the amount of hydrogen peroxide should be decreased instead of the amount of aniline. As far as the NASH product is concerned, a small amount was formed when the 1:1 solution, even less produced from the 1:3 solution, and the most from the 1:2 solution of aniline to hydrogen peroxide. It seems that when the amount of hydrogen peroxide is the same as the amount of aniline added, the aniline is not oxidized quickly enough to form the NASH product in large quantities. In fact, the abundance of azobenzene and azoxybenzene present is very small when compared to the other two samples. The 1:2 sample contains enough hydrogen peroxide to oxidize the aniline to nitrobenzene, but not enough to oxidize all of the aniline before it has time to couple with the azoxybenzene to form the NASH product. The 1:3 solution seems to be ideal for producing azoxybenzene considering the NASH product amount in collection three is minimal. This is due to the fact that enough hydrogen peroxide is great enough in the solution to oxidize most of the aniline to nitrosobenzene or nitrobenzene to couple with the excess aniline to form azobenzene or azoxybenzene. In this case, there is a very small amount of aniline left over for the formation of the NASH product. Essentially, it seems that the 1:1 solution is the most effective for forming azobenzene in high yields, the 1:2 solution is most effective for the production of the NASH product, and the 1:3 solution is most effective for azoxybenzene production. The goal, now, is to optimize the procedure
of the formation of azobenzene in high yields with minimal amounts of side products.

The GC column was then purged and the 1:1 aniline to peroxide solution was rerun through a new nanotube column and analyzed again. Different results were obtained this time with a clean column. The results are shown in Figures 39 and 40.

![Abundance Graph](image)

5.634 min represents azobenzene

**Figure 38.** GC spectrum of nanotube column collection

Figure 38 shows the GC spectrum of the first collection of 0.5 mL taken immediately after the sample was collected. It is obvious from this spectrum that the background is fairly clean and this is the sole product at a retention time of 5.634 min.
Figure 39. Mass spectrum of the first collection from the nanotube column.

The above mass spectrum shows the m/z of 182 which is the formula weight of azobenzene.

Figure 40. Reference mass spectrum of azobenzene.33
When comparing the mass spectrum in Figure 39 with the reference spectrum in Figure 40, a peak is present in our sample at a m/z of 93 that is not present in the reference. This peak comes from aniline that is present in the column. After 30 min, another 0.5 mL of solution was added to the nanotube column and analyzed. There were now two peaks present in the spectrum; the azobenzene peak which now only had a peak area of 5.11% and the NASH product which had a peak area of 94.89%. The third collection was taken at 1 hr and again, there was a very large amount of NASH product, 98.77%, and a very small amount of azobenzene, 1.23%. At 2 hr, there was 3.85% azobenzene and 96.15% of the NASH product in the sample. At 3 hr, the amount of azobenzene seemed to increase. In this case it was 6.18% whereas the NASH product was 93.82%, and the 4th collection yielded 4.49% azobenzene and 95.51% NASH product. The difference between this set of reactions and the previous set of reactions is that the solution is allowed to sit inside the nanotubes for 30 min to 1 hr; whereas before, the reaction was done immediately after the previous collection was taken. This allowed enough time for the solution that remained inside the tubes to oxidize to nitrobenzene, then form azoxybenzene and then the NASH product.

The 1:2 solution was also analyzed in the same manner with a very clean column. The first 0.5 mL collection resulted in two peaks, azobenzene with a peak area of 64.08% and 35.92% azoxybenzene. The second collection at 30 min resulted in five different peaks: hydroxylamine – 5.06%, nitrobenzene – 11.46%, azobenzene – 16.53%, azoxybenzene – 64.45% and a very small amount of NASH product. At 1 hr, only three peaks were present, 70% of the NASH product, 17% azoxybenzene and 12.44% azobenzene. The 4th collection at two hours yielded four different product peaks: the
NASH product – 50.36%, azoxybenzene – 20.59%, azobenzene – 18.42% and nitrobenzene at 10.62%. The three hour collection yielded again 3 product peaks: 64.47% NASH product, 15.01% azoxybenzene and 20.52% azobenzene. The final collection at 4 hrs also showed four product peaks: 69.21% of the NASH product, 8.05% azoxybenzene, 7.56% azobenzene and 4.69% nitrobenzene. Because the column is very clean and produces very neat spectra here, the first collection only contained the two products that are expected for this reaction, azobenzene and azoxybenzene. Like before, the amount of hydrogen peroxide is so great in comparison with the aniline that the aniline is oxidized to nitrobenzene before it can couple with more aniline to produce azobenzene.

The 1:1 aniline solution was also analyzed by UV-VIS and compared with the convection method and the control. The control in this case is the solution that is put through the nanotube column. The collection is compared to the control to ensure that there are no other product peaks.

![Graph](image)

**Figure 41.** UV-VIS analysis of nanomachine product.
The UV-VIS analysis is very similar to the convection method. The peak at 347 nm is apparent in the 0.5 mL collection. There is also a small peak at 510 nm indicative of the NASH product. The one major difference between the nanomachine collection and the convection controlled reaction is that the convection reaction has a larger peak at 410 nm than does the nanomachine collection. The 410 nm peak represents cis-azobenzene. This led to some optimism that the reaction was stereoselective; however, this was later found to be not so from the further UV-VIS analysis.

Even though there was only one product obtained in the first collection of the 1:1 aniline to peroxide reaction, there was still aniline in the reaction collection. In order to correct this, a Pasteur pipette was used as the support for the nanotube column. This was chosen because the capillary end of the Pasteur pipette is much smaller in diameter than the micropipette tip and it is longer. The solution would have a harder time finding crevasses or open areas to flow around the nanotubes and hopefully would be converted completely to azobenzene by diffusing into all of the nanotubes. Ideally, the column should not allow any solution to flow outside of the nanotubes.

The capillary end of the Pasteur pipette was packed with CNTs and 1 mL of the 1:1 aniline to peroxide solution was added to the top of the Pasteur pipette. Again, it was held vertically and the solution was allowed to flow through by gravity. The solution began to diffuse into the nanotubes and come down the column. The problem was that an air pocket generated where the CNTs separated from each other. When this occurred, the solution no longer flowed through the nanotubes. An attempt at applying pressure with a pipette bulb to force the liquid through the tubes was not successful as the nanotubes were forced out with the solvent. The second attempt was more successful. Here, the
nanotubes were packed in the Pasteur pipette to just above the capillary end to prevent air packets from forming. This time, the 1:1 aniline to peroxide solution was added to the column and collected; however, some nanotubes were collected with it. There are also some nanotubes collected when the micropipette tip is used; however, this collection contained almost twice as much more.

One of the problems with using the micropipette tip and the Pasteur pipette tip is that a small amount of the carbon nanotubes comes out with the collected product. The stability of the collected product is then in jeopardy. When the solution flows through the column, not all of the aniline is converted to product, so having nanotubes in the collection will allow it to continue to catalyze the reaction. In order to prevent this from occurring, a small amount of cotton was packed into the end of the Pasteur pipette. Above this, the nanotubes were packed and another piece of cotton was packed onto the top of the nanotubes. Less than 0.1mL of the solution was soaked up by the cotton, so, it did not affect the results of the reaction. To this column, 0.5 mL a solution consisting of 1 M aniline and 1 M hydrogen peroxide in acetonitrile was added. The product was collected in approximately 10 min and analyzed by UV-VIS. Again, there was a peak at 347 nm which was rather large compared to the micropipette tip indicating that the concentration of the azobenzene product is larger than using the micropipette tip. This could be caused by the longer column and longer time the reaction stays in the column. The cis-azobenzene peak was also present at 410 nm in very high concentrations compared to previous reactions. The NASH product at 510 nm was also present in roughly the same yields as previous reactions.

The collection from the nanomachine is less than 0.5 mL because some of the
solution remains inside the nanotubes. This usually equates to about eight drops collected. In order to examine the product by UV-VIS, five drops of the solution are placed in a quartz cuvette to which acetonitrile is added to make a total of 3 mL. The absorbance values must then be multiplied by 12 to determine the concentration of the azobenzene formed. This accounts for the small peaks that are seen when the nanomachine products are analyzed.

The next step was to determine whether the nanotubes could be filled up with aniline and then react with hydrogen peroxide that is added to the nanotube column afterwards. To determine this, two solutions were made: 1. 1 mM aniline in acetonitrile and 2. 0.5 mM hydrogen peroxide in acetonitrile. The support for the nanotube column is the Pasteur pipette with cotton at both ends. Approximately 0.5 mL of the aniline solution was added to the nanotubes and flowed through the column in 10 minutes. Once all of the drops had been collected, 0.5 mL of the hydrogen peroxide solution was then added. The drops were collected in approximately eight minutes and analyzed by UV-VIS. The visible color change that normally occurs was not apparent in this collection. There also was no peak at 347, 410 or 510 nm. These results show that this nanotube column cannot be used to hold aniline and react with the peroxide to form any product. What may have occurred is that the hydrogen peroxide solution, instead of mixing with the aniline solution inside the nanotubes, actually pushed this solution out of the nanotubes. Perhaps the nanotubes should have been allowed to dry before the peroxide was added to eliminate some of the solvent. This reaction was also performed by adding pure aniline to the column to see if the nanotubes would fill up. Unfortunately, aniline is too viscous to enter into the nanotubes on its own. The liquid stayed at the top of the
column and did not move through the tubes.

Hydrogen peroxide and carbon nanotubes may not be the only catalyst for the reaction. Excess dissolved oxygen or nitrogen in the solvent may also increase the rate of the reaction. In order to determine if this was happening, O₂ (g) and N₂ (g) were bubbled into separate vials containing acetonitrile 90 min each. The acetonitrile bubbled with O₂ (g) was then used in the aniline reaction, analyzed by UV-VIS and compared to the control. The spectra resemble the previous examples and can be seen in Figure 42. The N₂ (g)-bubbled acetonitrile was also used for the aniline reaction and analyzed by UV-VIS. These results can be seen in Figure 43. The reactions were performed in a sealed vial and the reactants were fed through by syringes so that the external environment did not affect the reaction.
Figure 42. Analysis of O$_2$ saturation of acetonitrile.
The results are very similar to each other with the exception that the N$_2$ saturated reaction seems to have produced more azobenzene than the O$_2$ saturated reaction. Two different nanotube columns were used for these reactions which will cause some variation in the amount of product. What this might suggest, however, is that neither oxygen nor nitrogen gas has any effect on the reaction and the oxidation of the aniline solely depends on the hydrogen peroxide.
4.2.2.1 Concentration Dependence of Aniline

Overall, it seems that the 1:1 aniline to peroxide ratio provides the best results for the nanomachine simulation with these reactants. Only one product was formed as indicated by the GC/MS data. Because azobenzene is the sole product for this reaction, it is proven that for this reaction, the nanomachine is successful. It was also determined from these experiments that the Pasteur pipette column is not a suitable support for the nanotube column and that the micropipette tip should be used for all future experiments. The attempts at trying to force the solution out of the Pasteur pipette column when the cotton was used as a filter resulted in the production of no azobenzene, indicating that it is important to allow the solution to diffuse into and out of the nanotubes on its own.

4.2.3 p-Toluidine Oxidative Reaction

*p*-Toluidine was also reacted with hydrogen peroxide using the nanomachine column. For all *p*-toluidine reactions, micropipette tips were used. Initial reactions were performed using a 1 M *p*-toluidine and 1 M hydrogen peroxide in acetonitrile solution that is run through the smallest micropipette tip column. The specifications for the *p*-toluidine system can be seen in Table 10.
Table 10. Specifications for p-Toluidine Reaction

<table>
<thead>
<tr>
<th>Nano column specifications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume of micropipet tip</td>
</tr>
<tr>
<td>Weight of nanotubes</td>
</tr>
</tbody>
</table>

1st addition of 0.5 mL
- Time for first drop: 36 s
- Time for first colored drop: ~2 min
- Time for all of solution to drop: 6 min 16 s

2nd addition 0.5 mL
- Time for first drop: 24 s
- Total time of collection: 8 min 59 s

3rd addition of 0.5 mL
- Time for first drop: 25 s
- Total time of collection: 10 min 11 s

4th addition of 0.5 mL
- Time for first drop: 30 s
- Total time of collection: 12 min 26 s

When comparing Table 8 and Table 10, it is obvious that the time for the p-toluidine reaction to flow through the nanotube column is considerable, longer than the aniline reaction. This could be due to the fact that p-toluidine, azotoluene and azoxytoluene are larger molecules than the previous reactants and products. The p-toluidine reaction also takes a longer time to produce a colored product, as in the case of the convection and kinetic mechanisms. This may indicate that even though the reactants are in close proximity to each other, they are less reacting than the reactants in the aniline system.

Unlike the aniline reaction, the concentrations of p-toluidine and hydrogen peroxide at a 1:1 ratio are not ideal for producing azotoluene as the sole product. The number of products found in GC/MS analysis from collection one is much larger than the aniline reaction. The following are the results that were performed on the same day with...
the same column settings as the aniline reaction that produced 100% azobenzene.

Table 11. GC/MS Analysis of p-Toluidine Collections

<table>
<thead>
<tr>
<th>Collection 1</th>
<th>Retention Time (min)</th>
<th>Peak Area (%)</th>
<th>Mass Number</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.59</td>
<td>1.43</td>
<td>28, 77, 94, 106, 123</td>
<td>4-hydroxylaminotoluene</td>
<td></td>
</tr>
<tr>
<td>4.39</td>
<td>8.42</td>
<td>28, 77, 106, 135</td>
<td>4-nitrotoluene</td>
<td></td>
</tr>
<tr>
<td>7.04</td>
<td>16.4</td>
<td>65, 91, 119, 165, 210</td>
<td>azotoluene</td>
<td></td>
</tr>
<tr>
<td>8.14</td>
<td>37.76</td>
<td>65, 77, 91, 105, 226</td>
<td>azoxytoluene</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Collection 2</th>
<th>Retention Time (min)</th>
<th>Peak Area (%)</th>
<th>Mass Number</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.59</td>
<td>0.28</td>
<td>28, 77, 94, 106, 123</td>
<td>4-hydroxylaminotoluene</td>
<td></td>
</tr>
<tr>
<td>4.42</td>
<td>9.15</td>
<td>28, 77, 106, 135</td>
<td>4-nitrotoluene</td>
<td></td>
</tr>
<tr>
<td>6.77</td>
<td>22.74</td>
<td>91, 180, 197</td>
<td>Not identified</td>
<td></td>
</tr>
<tr>
<td>7.05</td>
<td>18.73</td>
<td>65, 91, 119, 165, 210</td>
<td>azotoluene</td>
<td></td>
</tr>
<tr>
<td>8.14</td>
<td>34.28</td>
<td>65, 77, 91, 105, 226</td>
<td>azoxytoluene</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Collection 3</th>
<th>Retention Time (min)</th>
<th>Peak Area (%)</th>
<th>Mass Number</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.58</td>
<td>0.99</td>
<td>28, 77, 94, 106, 123</td>
<td>4-hydroxylaminotoluene</td>
<td></td>
</tr>
<tr>
<td>4.4</td>
<td>6.27</td>
<td>28, 77, 106, 135</td>
<td>nitrotoluene</td>
<td></td>
</tr>
<tr>
<td>6.77</td>
<td>19.13</td>
<td>91, 180, 197</td>
<td>Not identified</td>
<td></td>
</tr>
<tr>
<td>7.04</td>
<td>23.97</td>
<td>65, 91, 119, 165, 210</td>
<td>azotoluene</td>
<td></td>
</tr>
<tr>
<td>8.15</td>
<td>39.51</td>
<td>65, 77, 91, 105, 226</td>
<td>azoxytoluene</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Collection 4</th>
<th>Retention Time (min)</th>
<th>Peak Area (%)</th>
<th>Mass Number</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.59</td>
<td>1.05</td>
<td>28, 77, 94, 106, 123</td>
<td>4-hydroxylaminotoluene</td>
<td></td>
</tr>
<tr>
<td>4.4</td>
<td>5.45</td>
<td>28, 77, 106, 135</td>
<td>nitrotoluene</td>
<td></td>
</tr>
<tr>
<td>6.77</td>
<td>16.65</td>
<td>91, 180, 197</td>
<td>Not identified</td>
<td></td>
</tr>
<tr>
<td>7.06</td>
<td>29.65</td>
<td>65, 91, 119, 165, 210</td>
<td>azotoluene</td>
<td></td>
</tr>
<tr>
<td>8.16</td>
<td>38.45</td>
<td>65, 77, 91, 105, 226</td>
<td>azoxytoluene</td>
<td></td>
</tr>
</tbody>
</table>

Table 11 shows only the most abundant of the peaks with the exception of 4-hydroxylaminotoluene. This product peak is shown to give further support to the proposed mechanism. 4-Hydroxylaminotoluene was not present in the analysis originally. The largest amount of product in all collections is clearly azoxytoluene whose peak area remains approximately the same throughout the entire experiment. The azotoluene peak
increases, up to 30% of the total product, as the amount of solution fed into the nanotube column increases. The amount of nitrotoluene decreases as the experiment goes on indicating that azoxytoluene is being formed in larger quantities. To counteract the loss of the nitrotoluene and provide a reason why the peak area of the azoxytoluene stays the same if in fact the concentration increases, a new peak appears with a retention time of 6.77 min. This peak has not been identified but is a substantial product. The molecular weight of 197 g/mol indicates that it must be occurring before the coupling of nitroso- or nitrotoluene with p-toluidine. Even with the large amount of product formation, it is apparent that azoxybenzene is the major product of the reaction of 1 M p-toluidine with 1 M hydrogen peroxide in acetonitrile.

This reaction was then analyzed by UV-VIS absorption spectroscopy. Although the dark red-orange product was formed after 2 min, there was no peak found in the analysis probably due to the fact that only two drops were collected which were dissolved in 3 mL of acetonitrile. Figure 44 compares the control and collection spectra. No product peaks are apparent in either sample.
Figure 44. UV-VIS spectra of \( p \)-toluidine collection vs. control for 1 M : 1 M solution.

In order to determine whether the UV-VIS spectrum for the CNT column method is comparable to convection method, a solution consisting of 2 M \( p \)-toluidine and 1 M hydrogen peroxide in acetonitrile was made. 0.75 mL of this solution was added to the
CNT column and five drops were collected in 5.5 min. The five drops were then dissolved in 3 mL of acetonitrile and analyzed by UV-VIS spectroscopy. As expected, a peak appears at 462 nm from the collected solution representing azotoluene as is shown in Figure 45. The control solution produced no peak in this range.

![Figure 45. UV-VIS spectra of p-toluidine collection vs. control for 2M p-toluidine and 1M hydrogen peroxide.](image-url)
In order to determine the optimum conditions for this reaction, a series of solutions were made containing 1 mM – 5 mM p-toluidine and 1 M hydrogen peroxide in acetonitrile. Each of the solutions was added to a separate nanotube column in 0.75 mL portions. Five drops of the product were then diluted in 3 mL of acetonitrile and analyzed by UV-VIS. The absorption spectra are shown in Figure 46.

![Figure 46. p-Toluidine concentration dependence on azotoluene peak.](image)

It is obvious that the 5 M p-toluidine solution has the highest absorbance at 464 nm. The
absorption values were then tabulated and the concentrations of azotoluene for each were determined using Beer's Law. The results are shown in Table 12.

Table 12. Concentration of Azotoluene in Samples with Varying Concentration of \( p \)-Toluidine

<table>
<thead>
<tr>
<th>( C_{p\text{-toluidine}} ) (initial-M)</th>
<th>( C_{\text{peroxide}} ) (initial-M)</th>
<th>Absorbance</th>
<th>Extinction Coefficient</th>
<th>( C_{\text{azotoluene}} )</th>
<th>Correction Factor</th>
<th>Actual ( C_{\text{azotoluene}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>1</td>
<td>1.033</td>
<td>5.62E+02</td>
<td>1.84E-03</td>
<td>12</td>
<td>2.21E-02</td>
</tr>
<tr>
<td>2.5</td>
<td>1</td>
<td>0.351</td>
<td>5.62E+02</td>
<td>6.25E-04</td>
<td>12</td>
<td>7.49E-03</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>0.257</td>
<td>5.62E+02</td>
<td>4.57E-04</td>
<td>12</td>
<td>5.49E-03</td>
</tr>
<tr>
<td>0.5</td>
<td>1</td>
<td>0.218</td>
<td>5.62E+02</td>
<td>3.88E-04</td>
<td>12</td>
<td>4.65E-03</td>
</tr>
<tr>
<td>0.25</td>
<td>1</td>
<td>0.082</td>
<td>5.62E+02</td>
<td>1.46E-04</td>
<td>12</td>
<td>1.75E-03</td>
</tr>
<tr>
<td>0.1</td>
<td>1</td>
<td>0.059</td>
<td>5.62E+02</td>
<td>1.05E-04</td>
<td>12</td>
<td>1.26E-03</td>
</tr>
<tr>
<td>0.05</td>
<td>1</td>
<td>0.18</td>
<td>5.62E+02</td>
<td>3.20E-04</td>
<td>12</td>
<td>3.84E-03</td>
</tr>
<tr>
<td>0.01</td>
<td>1</td>
<td>0.048</td>
<td>5.62E+02</td>
<td>8.54E-05</td>
<td>12</td>
<td>1.02E-03</td>
</tr>
<tr>
<td>0.005</td>
<td>1</td>
<td>0.032</td>
<td>5.62E+02</td>
<td>5.69E-05</td>
<td>12</td>
<td>6.83E-04</td>
</tr>
<tr>
<td>0.001</td>
<td>1</td>
<td>0.031</td>
<td>5.62E+02</td>
<td>5.52E-05</td>
<td>12</td>
<td>6.62E-04</td>
</tr>
</tbody>
</table>

It is apparent from Table 12 that the higher the concentration of the \( p \)-toluidine starting material, the higher the concentration of azotoluene formed. This occurs with only a few exceptions. These values give %yields of azotoluene in the range of 20-50%. These values vary depending on the column differences in each of the experiments. The actual %yield will also be higher than these values suggesting that the product that is left in the nanotubes and not collected. One of the highest %yield values found was 46% for the 0.1-M \( p \)-toluidine sample. This concentration of \( p \)-toluidine was then used to determine the optimum conditions for the reaction. The values obtained can be seen in Table 13.
The hydrogen peroxide acts in the same way as p-toluidine in that the more hydrogen peroxide present in the starting reaction, the more azotoluene is found in the collection. In this case, the % yield values range from 21-51%. The 0.1 M p-toluidine/1 M hydrogen peroxide solution produces the most azotoluene with a yield of 51%. This is the highest %yield obtained and it was determined that these conditions would be optimal for the highest yield of azobenzene as determined by this method.

Having optimum conditions for the production of azotoluene, the %conversion of p-toluidine was then determined. The experiment was designed in such a way that the p-toluidine peak at 296 nm was monitored for both the control solution and the collection. A solution of 0.01 M p-toluidine and 1M hydrogen peroxide in acetonitrile was made and 0.75 mL was placed in the CNT column. Five drops of each, the control and the collection, was added to 3 mL of acetonitrile and analyzed by UV-VIS. The results can be seen in Figures 47 and 48.
Figure 47. %Conversion of p-toluidine 296 nm peak.

Figure 48. Azotoluene formation in nanomachine.

Figure 48 shows the difference in the 296 nm p-toluidine peak between the control solution and the collected sample. The amount of p-toluidine converted in the reaction is determined by the difference in absorbance between the two spectra at 296 nm. This absorbance difference is used in Beer’s Law to determine the concentration of p-toluidine.
used. Figure 49 shows how much azotoluene was formed during the reaction. The conversion efficiency of the CNT column was then determined using the following equation:

\[
\text{Conversion efficiency} = \frac{C_{\text{azotoluene}}}{(0.5 \times \Delta C_{\text{p-toluidine}})} \quad \text{(Eq. 3)}
\]

The mechanism of the reaction requires two \( p \)-toluidine molecules to form one azotoluene molecule. Table 14 indicates the conversion efficiency for three different CNT columns.

<table>
<thead>
<tr>
<th>( \Delta ) (296nm peak)</th>
<th>Cp-toluidine</th>
<th>A (464nm)</th>
<th>Cazotoluene</th>
<th>Conversion Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.757</td>
<td>3.29E-04</td>
<td>0.048</td>
<td>8.54E-05</td>
<td>51.90</td>
</tr>
<tr>
<td>0.473</td>
<td>2.06E-04</td>
<td>0.056</td>
<td>9.96E-05</td>
<td>96.91</td>
</tr>
<tr>
<td>0.477</td>
<td>2.07E-04</td>
<td>0.055</td>
<td>9.79E-05</td>
<td>94.38</td>
</tr>
</tbody>
</table>

*10 mM \( p \)-toluidine and 1 M hydrogen peroxide in acetonitrile

As is the case when determining the concentration of azotoluene formed, the column conversion efficiency depends largely on the packing of the carbon nanotube column. If the CNT column is not packed efficiently, the solution will travel around the tubes and the azotoluene product will not be in high yield. In this case, the column efficiency varies between 51.8 and 96.9% conversion of \( p \)-toluidine to azotoluene. In the ideal system, the conversion efficiency would be 100%. The second CNT column shown in Table 14 is the closest to ideal at 96.9% conversion. All of the evidence above supports the theory that a CNT column will provide high-yield synthesis of azotoluene and azobenzene depending on the starting material.
4.2.4 Methylamine Reaction.

A carbon nanotube column was configured that was 1.125" long and 0.0625" in diameter using a Pasteur pipette. 0.23 mL methylamine and 1 mL H$_2$O$_2$ were added to acetonitrile to make a total volume of 10 mL. 0.75mL of this solution was then added to the pipette filled with carbon nanotubes. Within 2 minutes, 1 drop was collected. There was no color change or heat produced within this time frame. Immediately after the first drop was collected, the reaction began to turn warm and bubbles rose up through the nanotubes and the solution above them at a constant rate for over 30 minutes. The solution that had entered into the nanotube column never flowed through the column to be collected. The heat evolved during the reaction was measured by using a thermocouple placed on the outside of the glass of the column. The initial temperature was measured to be 26.0 °C. After five drops of the methylamine/peroxide solution were added to the column, the temperature of the glass increased to 26.9 °C and then slowly went back down to approximately 26.1 °C. This is not the temperature of the solution because it was virtually impossible to measure the temperature of the solution inside the Pasteur pipette. If azomethane is formed as a product, it probably could not be collected because it is a gas.

4.2.5 Oxidation of Diphenylamine

The oxidation of the secondary aromatic amine follows similar reaction course to that of $p$-toluidine. The oxidation by hydrogen peroxide (0.1 M diphenylamine and 0.1 M hydrogen peroxide) produces a rapidly changing colored product in the presence of carbon nanotubes. Figure 50 shows the visible absorption spectrum with a maximum at
432 nm. In the absence of the carbon nanotubes, there is no 432 nm peak.

The GC/MS spectrum in the two situations shows the following features: when the reaction is carried out in the column configuration, the collected solution showed retention times of $t_r=5.31$ min, corresponding to m/z of 183, 154, 129 and 103. and $t_r=6.04$ min, corresponding to a m/z of 185. The peak with a m/z of 183 could be identified as $C_6H_5NH-N=C_6H_5$ with a byproduct corresponding to a biphenyl fragment. The parent species responsible for $t_r=5.31$ min is due to the above hydrazo linkage which accounts for the 432 nm peak in the UV-VIS spectrum. The m/z of 185 is attributed to the species $(C_6H_5)_2$ NOH. This could be the result of the formation of hydroxylamine in

Figure 49. Nanomachine collection from diphenylamine reaction.
the primary step of the oxidation reaction. When the control solution is examined, only the hydroxide species is observed in the GC/MS as a common entity. No hydrazo compound is obtained. Also, the absorption spectrum of the control solution does not show any peak (see Figure 49). It appears that carbon nanotubes are acting in the same way as was observed with primary aromatic amines.

4.3 Relevance of Nanosynthetic Machine Concept in Relation to the Existing Technology

There are many different ways of producing azobenzene that are used in commercial processes today. Diazotization involves the preparation of a diazonium salt of aniline and reacting with liquid benzene. This method is very expensive, the materials cannot be regenerated and large amounts of salts are obtained [34, 35, 36]. Another method involves the reduction of nitrobenzene without the use of a catalyst but requires high heat (250°C) and pressure (3000 atm) to produce a 97.5% yield in 24 hr [37]. When nitrobenzene is reduced in the presence of a metal catalyst, such as CO (g), NO (g) or SO₂ (g), a relatively low yield of product is formed [38, 39]. This method also includes the use of high heat and forms byproducts such as nitrosobenzene and azoxybenzene. Nitrobenzene can also be deoxygenated to azobenzene in the presence of a catalyst, such as K$_2$CO$_3$, which results in the breakdown of the catalyst by oxidation [40]. In all of these cases where a catalyst is used, it cannot be regenerated. When functionalized carbon nanotubes are used as the catalyst, very high yields of azo compounds are formed in very short time periods (5-10 min). The aniline reaction produces 100% azobenzene when the CNT column is used, and, the p-toluidine reaction produces 50-97% azotoluene in that time frame. The lower yields in the p-toluidine reaction are due to the carbon
nanotube column and will be alleviated when the nanomachine is built. Because the catalyst is kept in a support and not mixed with the reaction, it does not need to be filtered or regenerated and can be reused. Once the nanomachine is developed, the solution will have to flow through the nanotubes and 100% azo product yield and 100% conversion should be found at all times.

5. Conclusions

The oxidation of primary and secondary amines by hydrogen peroxide in the presence of functionalized carbon nanotubes was examined for the formation of azo compounds. In all cases, when the functionalized carbon nanotubes are not present, the azo product is not formed. It was determined that functionalized multiwalled carbon nanotubes act as catalysts for the formation of azobenzene, azotoluene, an azobenzene salt and possibly azomethane were formed when aniline, p-toluidine, diphenylamine and methylamine, respectively, were used as the starting materials. The formation of azomethane could not be conclusively determined to be the product in the methylamine reaction because it has the same mass number as the solvent, acetone. Because the molecules are held in close proximity of each other, they form products that they cannot be formed in the control solution without high heat and long periods of time.

The initial experiments were performed with the solutions in a reaction vessel and the functionalized nanotubes either sitting at the bottom of the reaction flask or being stirred while the reaction is occurring. This method produced that desired azo compound, but also undesired azoxy, nitro and nitroso compounds. These products are also formed
in the control solution, without the nanotubes. This indicates that the azoxy, nitro and nitroso compounds come only from the outside solution and are not formed inside the nanotubes. The products were analyzed by GC/MS and UV-VIS absorption spectroscopy to determine the content of the solutions.

In order to eliminate the undesirable products, a nanomachine consisting of aligned carbon nanotubes on a support, was conceived and simulated. The simulation involved filling micropipette tips and Pasteur pipettes with functionalized carbon nanotubes, adding the reaction solution and allowing it to flow through by gravity. The collected sample was analyzed by GC/MS and UV-VIS and determined to be 100% for azobenzene and 50-97% for azotoluene in the oxidation of aniline and p-toluidine respectively.

Essentially, the carbon nanotube column has the ability to produce very high yields of a product that is unique to the system in a relatively short period of time. This process would be very useful for the production of azobenzene and other azo compounds and is an insight into the world of nanodimensional reactions.
6. References

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30. a.) Lide, D. CRC Handbook of Chemistry and Physics, 78th Edition, CRC Press,


