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CONVERSION OF ANILINE TO AZOBENZENE AT FUNCTIONALIZED CARBON NANOTUBES: A POSSIBLE CASE OF A NANODIMENSIONAL REACTION

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ABSTRACT

Aniline is oxidized to nitrosobenzene as the initial product, which undergoes further oxidation to nitrobenzene. The nitrosobenzene formation is catalyzed by functionalized multiwalled carbon nanotubes (CNT) followed by a coupling reaction between nitrosobenzene and aniline to produce azobenzene. This coupling requires close proximity of the reactants. It proceeds rapidly resulting in the UV-VIS absorption spectrum showing maxima at 327 nm and 425 nm. The nitrosobenzene yield in the presence of CNTs is controlled by the amount present in the medium. As the reaction is not catalyzed by multiwalled CNTs in this catalysis suggests a nano dimensional reaction pathway.

Key words: Aniline, hydrogen peroxide, carbon nanotube, TEM, azobenzene, azoxybenzene, acetonitrile, acetone, functionalized CNT, nitroso- benzene, nitrobenzene, GC/MS and TGA.

1. Introduction

The oxidation of aniline has been carried out under widely varying conditions to yield a large number of products¹⁻¹⁰. Among these oxidations, the one using hydrogen peroxide is interesting in the light of solvent, time and temperature dependent evolution of different product²⁻⁶. The importance of this oxidation arises as a precursor for the vulcanization of rubber, removal of pollutants in waste water and antioxidant in lubricating oil¹¹⁻¹³. The oxidation most often requires catalysts; the catalysts range from metallic ions such as ferrous to others such as manganese dioxide, titanium silicate molecular sieves and clathrates. With some of the catalysts, selective oxidation of aniline has been proposed⁶.

Multiwalled CNTs are structurally interesting materials having diameters in the range of 30-40 Å and lengths of nm to μm¹⁴. The tubular structure of the CNTs provides an opportunity to carry out chemical reactions inside the narrow (nano) dimensions of the tube. Remarkable results have been obtained earlier by carrying out several inorganic chemical reactions inside the tubes¹⁵⁻¹⁸, which resulted in metallic deposits being formed inside the tubes. These deposits have been examined by transmission electron microscopy. The CNTs have also been proposed for hydrogen storage¹⁹⁻²². Other modifications of the CNTs have been successful in enantio-separations²³. Multiwalled CNTs have been successfully used as electrodes for electrochemical investigations²⁴⁻²⁷.

A nano dimensional reaction is defined as the one, which occurs in a space of a nm diameter and a length of a nm or higher where the reactants, and products are present in these narrow dimensions. We wish to report here the catalyzed oxidation of aniline with hydrogen peroxide by purified functionalized multiwalled CNTs; this reaction proceeds extremely slowly in the absence of the CNTs. In its presence the reaction is spectacular as a colored product emanates from the CNTs slowly fills up the outside solution by diffusion. The reaction product is monitored by using UV-VIS spectrophotometry. The UV-VIS spectrophotometry can be used to understand the nature of the reaction. This is probably the first case of an organic reaction being catalyzed by the functionalized CNTs. This oxidation should be of interest in the preparation of conducting polymer composites²⁶ and in mechanistic understanding of the formation of polyaniline at CNT²⁷

2. Experimental

2.1 Chemicals and Instruments

Aniline (Aldrich) was purified by distillation. The fraction boiling at 180° C was collected, sealed and kept in the refrigerator until further use. Hydrogen peroxide (30% vol/vol) (Baker analytical grade) was used in the experiments.

UV-VIS absorption spectra were recorded using Shimadzu UV2000 series spectrophotometer. Helwett-Packard GC-MS (HP 6890 series with HP 5973 Mass selective detector fitted with Agilent (19091S-396)) and Bio-Rad FTIR spectrometer (Excalibur series) were used in the experiments. SEM pictures were recorded at RPI .

2.2 Functionalization of Carbon Nanotubes

A known quantity of multiwalled carbon nanotubes (Deal International or Strem Chemicals) was taken in a round-bottomed flask. In some experiments, laboratory (RPI) synthesized multiwalled CNTs by arc discharge method were used. Following the procedure of Green et al¹⁶, the required quantity of nitric acid was added to the round-bottom flask. The mixture was refluxed for a period ranging from 6-24 h. The CNTs were taken out by filtration and washed with running distilled water for 2 h. The resulting sample was refluxed in 50 ml of distilled water for a period of 24 h. The CNTs were taken out by filtration and dried at 100° C for 24h. The functionalized CNTs were characterized by IR, TGA, TEM and XRD.

IR spectra were recorded using Fourier Transform Infrared Spectrometer (BIO RAD) showed well-defined peaks at about 1820 cm⁻¹ and 1700 cm⁻¹. These peaks are attributed to the C=O functionalization of the multiwalled CNTs. These peaks were absent in the unfunctionalized CNTs.

TGA was carried out using a TA instrument (Delaware). The experiments were performed under purified nitrogen atmosphere or in air using functionalized CNT. The instrument has the capability of obtaining mass changes in the range of 5 µg to 100 g. Under nitrogen atmosphere the sample showed no appreciable weight loss upto about 1000°C. In the absence of nitrogen atmosphere (in air), the weight percent starts to decrease at about 600°C and reaches 0% at about 890°C as shown in Figure 1. This weight loss is attributed to the conversion of nanotubes to CO₂. It also suggests that there is no residue metallic or non-metallic remaining above this temperature. TGA

experiments carried out with unfunctionalized CNT showed a similar weight loss but occur at about 720°C. The TGA experiments carried out in the presence of nitrogen showed a weight loss of only about 8% at 1000°C; this is in comparison to the loss that occurs in the presence of oxygen which is at 100%.

TEM of functionalized CNT showed characteristic nanotubular opened structure. XRD analysis of the sample showed one 2theta reflection at 24.4°.

Atomic absorption spectroscopy (AAS) experiments were completed using Perkin-Elmer AA100 for metal ion determination in the CNT. For this experiment, 60 mg of functionalized CNTs was sonicated in 10 ml acidified distilled water for about one hour and the resulting solution taken for the determination of metals like Cu and Fe. In both the experiments, no detectable signals were obtained above the background suggesting the absence of these metals in functionalized CNTs.

2.3 pH of CNT solutions:

60 mg of CNTs is added to distilled water. The solution was sonicated for about an hour and the pH of the solution determined. The pH value was very little affected by the CNT.

2.4 Procedure

A known volume of aniline (1 ml to 5 ml) was taken into a reaction vessel and to which a weighed amount of functionalized CNTs was added to it. A known volume of acetonitrile or acetone (adjusted to 10 ml) was added into this reaction vessel and agitated for several minutes. After allowing the CNTs to settled down in the reaction vessel, a required volume of hydrogen peroxide (in the mole ratio of aniline to hydrogen peroxide ranging from 0.1 to 5.0) was added and stirred. The resulting solution was taken for analysis by GC-MS and UV-VIS absorption spectrophotometry. All experiments were carried out at ambient temperature.

For studying the aniline oxidation at elevated temperature, a round-bottomed flask fitted with Leibig condenser was used. With an inert gas, nitrogen, flowing through the reaction vessel, the reaction was carried out for an hour. The reaction mixture was analyzed by GC-MS or UV-VIS spectrophotometry.

3. Results and Discussion

To explore the catalysis of functionalized multiwalled CNTs, aniline oxidation is carried out with aniline/peroxide mole ratio of 1.0 in the presence of 40 mg of functionalized CNTs for a time period of one hour. The solution, which is colorless in the beginning slowly turned orange red with color gradients existing in the solution from the CNT to the bulk of the solution. An aliquot (1-5 µl) of the solution is taken out for GC-MS analysis. The GC MS showed peaks at $m/z = 108, 77, 51$ and 50 . The control for these experiments is also done without the CNTs. The results of the GC-MS are analyzed for the products as shown in Table 1. The initial product of the oxidation is nitrosobenzene in both cases. In the presence of the functionalized CNTs, the yield of nitrosobenzene is higher as shown in the Table 1. As the reaction progresses over several hours, distinct changes in the color of the solutions have been noticed; the one with functionalized CNTs

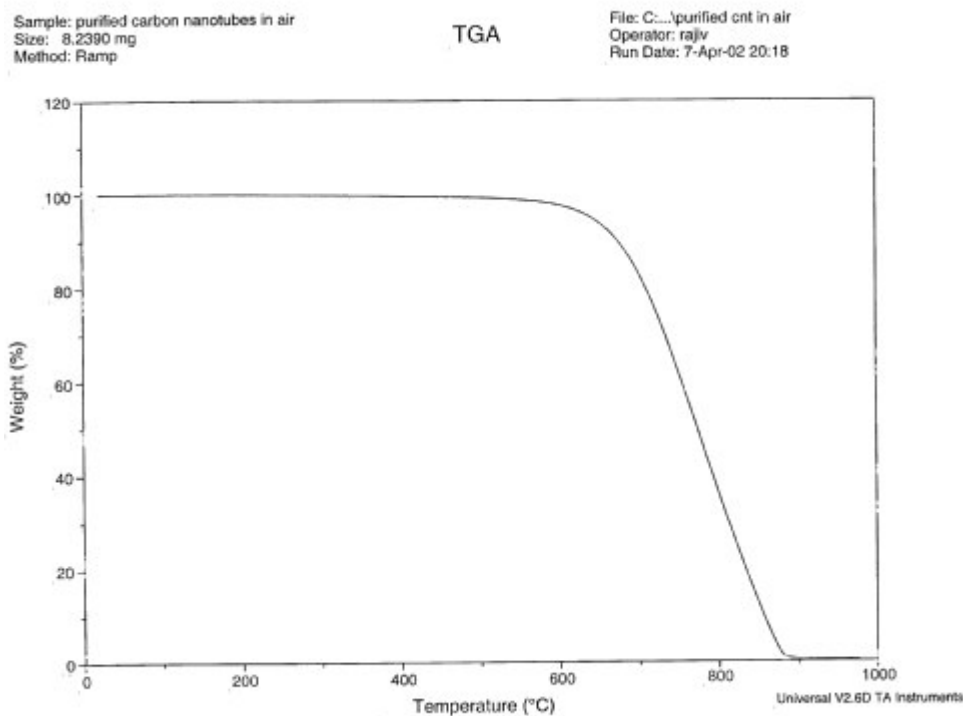


Fig1: Thermogravimetric analysis of functionalized multiwalled carbon Nanotubes

generating a reddish product diffusing into the solution. Note that the density of the multiwalled CNT is about 1.6-1.8²⁴⁻²⁶ and hence it settles down at the bottom. In the experiments carried out without the CNT, the yield of nitrosobenzene is less as shown in data in Table 1. When the experiments are carried out with larger quantity of functionalized CNTs in the medium, an increase in the product yield is observed.

Table 1: Catalysis of Functionalized CNTs

Mole Ratio	Aniline converted (%)	Nitrosobenzene Yield (%)
1	4.94	21.86
1 ^a	3.40	38.23
5	2.19	34.24
5 ^a	1.62	58.64

a. 40 mg of CNT catalyst; At 1 h after the start of the reaction

3.1 Coupling of Nitrosobenzene and Aniline

The first step in the oxidation process appears to be the formation of nitroso benzene⁴⁻¹⁰ and a higher yield of it has been noticed in the presence of functionalized CNTs.

As the reaction progresses, GC-MS showed m/z = 181,105,77,51 and 50 which could be fitted into the characteristic pattern of fragmentation of azobenzene. The formation of azobenzene could be visualized as due to the coupling reaction of nitrosobenzene with aniline. Without the CNTs in the medium, the coupling reaction is not observed. The orange red solution has been characterized by in situ UV-VIS absorption spectroscopy.

An absorption maxima at 327 nm and 425 nm appears which grows with time. In the absence of the CNTs, these peaks are distinctly absent.

The progress of the reaction in the three situations-A) control with no functionalized CNTs , B) identical solution with functionalized CNTs (opened nanotubes- and C) identical solution with non-functionalized CNTs.

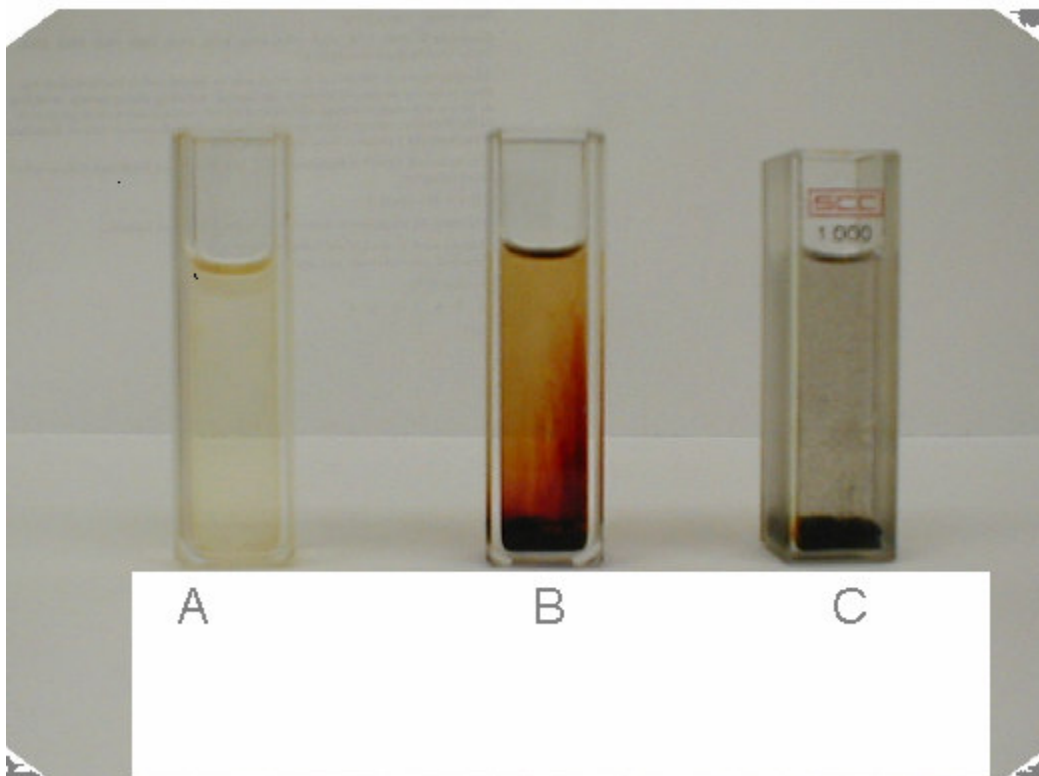


Fig. 2 Visual demonstration of the aniline oxidation at functionalized CNTs.

The photograph was taken at 15 minutes of the start of the reaction. Note that in cuvette B, the setting up of the density gradient, which has been followed by in situ UV-VIS absorption spectrophotometry. The product of the reaction is visualized as flowing out of the CNTs as shown in Figure 2. The absorption spectral features in the three solutions are characteristically different as discussed earlier. These differences arise from the functionalized tubes providing the pathway for the oxidative reaction; it is not very clear as to the exact mechanism by which this happens. TEM pictures of the functionalized CNTs showed open ends along with some tubes having opening in the middle. The driving force for the reactants to enter the surface of the CNTs appears to be the carbonyl group. The reactants could be on this short nano dimensional surface for the reaction to occur either with or without entering into the tube. The CNTs, which are placed without functionalization, failed to produce the oxidative product (see Figure 2-C). Thus graphitic surface of the CNT alone does not show catalysis.

3.2 Effect of CNT on Optical Density

The optical density at 327 nm has been followed as a function of the amount of functionalized CNTs in the reaction vessel. It showed a progressive increase with increasing amount of CNT. Figure 4 shows the magnitude of increase in optical density.

It suggests that the reaction is dependent on the number of tubes present; however, in our experiments the number of tubes is not homogeneously present to draw inferences on the quantitative nature of the reaction.

3.3 Extraction of Products from CNT-Suggestive Evidence

One positive evidence that could be used in support of the oxidative reaction of aniline occurring inside the CNTs is from the extraction of the products from CNTs. After carrying out the aniline oxidation for a period of 24 hours, the solution is filtered and the CNTs are washed thoroughly several times with the solvent (acetonitrile or acetone). The solution obtained did not produce 327nm and 425 nm peaks indicating the absence of an adsorbed material on the CNTs. However, if the solution is sonicated in acetonitrile or acetone for one hour, the characteristic peaks at 327 and 425 nm of azobenzene are observed. It has been demonstrated earlier that an entrapped solution in CNTs could be displaced by repeated sonication by the development of thermal gradients. The above experiment demonstrates such a displacement. The solution showed photoisomerization; upon exciting the solution at 327 nm for one hour, the optical density of the peak at 425 nm increased. This change is reversible. Azobenzene has previously been demonstrated to undergo photoisomerization from trans to cis form and the results are in conformity with the above observation.

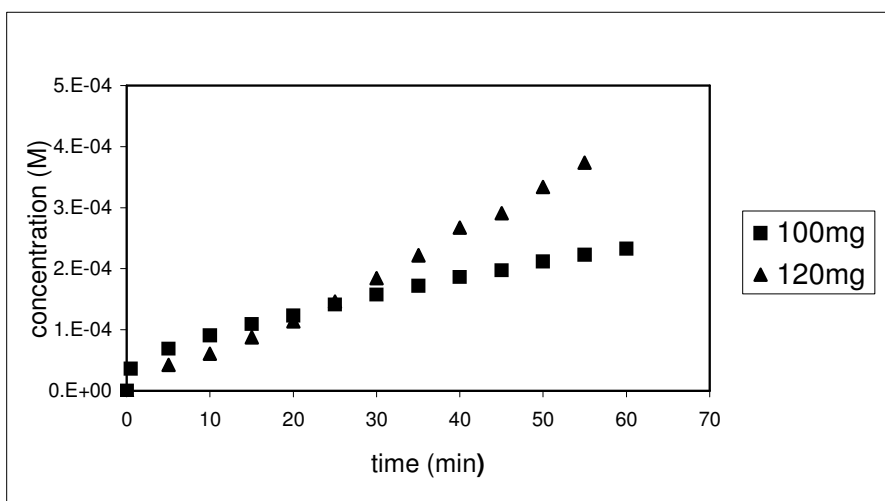
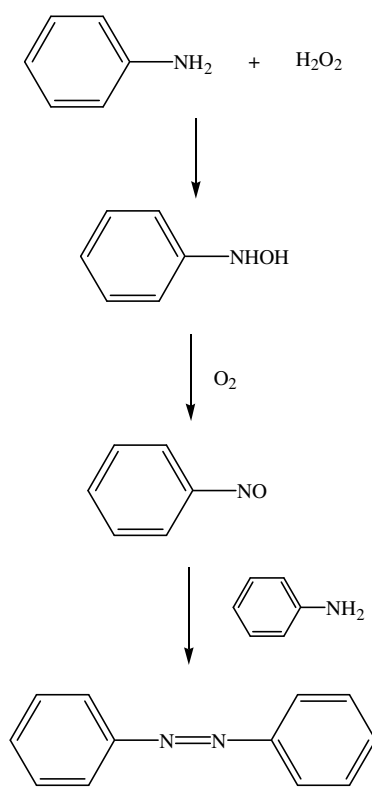


Fig 4: Concentration of azobenzene formed with different amounts of functionalized CNTs.

3.4 Proposed Reaction Mechanism

Aniline oxidation in acetonitrile or acetone is controlled by the presence of functionalized CNTs in the medium. The following reaction pathway is proposed



for the coupling of aniline with nitrosobenzene, functionalized CNTs are necessary as otherwise further oxidation of nitrosobenzene to nitrobenzene is a favored pathway. Thus the functionalized CNT appears to provide a mechanism of bringing the two reactants to a close proximity for this reaction to occur. One possibility is that the reactants are confined in the nanodimensional space of the functionalized CNTs. In general, the entropy factor limits this to occur in the unfunctionalized CNTs. The polarized nature of the carbonyl groups present on the functionalized CNT serves to overcome this limitation. Further work is in progress in order to understand more about the reactions with functionalized CNTs.

Table 2 gives the observed visual colorations in the oxidation of aniline with hydrogen peroxide.

Table 2: Product colors in the oxidation of aniline with hydrogen peroxide^a

Conditions	Color*	O.D. at 327 nm & 425 nm
With 60 mg functionalized CNTs	Orange-red	1.50, 1.02
Without functionalization	Colorless	0
Graphite	Colorless	0

- a. Reaction carried out with mole ratio of aniline to peroxide equal to one
* At 1 hour.

The distinctly different activity of functionalized CNTs is indicated by the data in Table 2. We propose this sensitive reaction for use in analytical determinations of aniline. It is however, not clear if any nanoparticles of graphite are participating in the nanodimensional reaction. It is hoped to resolve this by carrying out experiments using aligned multiwalled functionalized carbon nanotubes.

4. Conclusions:

The functionalized CNTs seem to have potentialities for bringing about oxidative reactions with aniline. The initial product of the oxidation is nitrosobenzene which couples with aniline to produce azobenzene. This reaction occurs only when functionalized CNTs are present in the medium. The nano dimensionality of the CNTs appears to provide confinement pathways to produce azobenzene as the product. The results suggest the possibility of developing nano synthetic machines with functionalized CNTs.

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