

2002

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CATALYZED OXIDATION OF ANILINE BY HYDROGEN PEROXIDE IN THE PRESENCE OF CNTS: A POSSIBLE CASE OF A NANODIMENSION REACTION

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ABSTRACT

The oxidation of aniline by hydrogen peroxide produces 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 reaction proceeds rapidly resulting in the UV-VIS absorption spectrum showing a 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 unfunctionalized CNTs or graphitic particles, the uniqueness of the functionalized multiwalled CNTs in this catalysis suggests a nano dimensional reaction pathway.

INTRODUCTION

The oxidation of aniline has been carried out under widely varying conditions to yield a large number of products (1-10). Among these oxidations, the one using hydrogen peroxide is interesting in the light of solvent, time and temperature dependent evolution of different products (2-6). The importance of this oxidation arises as a precursor for the vulcanization of rubber, removal of pollutants in waste water and antioxidant in lubricating oil (11-13). 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 proposed (6).

Multiwalled CNTs are structurally interesting materials having diameters in the range of 30-40 Å and lengths of nm to μm (14). The tubular structure of the CNTs provides an opportunity to carry out chemical reactions inside the narrow dimensions of the tube. Remarkable results have been obtained earlier by carrying out several inorganic chemical reactions inside the tubes (15-18) 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 storage (19-22). Other modifications of the CNTs have been successful in enantio-separations (23). Multiwalled CNTs have been successfully used as electrodes for electrochemical investigations (24-27).

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 composites (26) and in mechanistic understanding of the formation of polyaniline at CNT (27).

EXPERIMENTAL

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 .

Functionalization of Carbon Nanotubes

A known quantity of multiwalled carbon nanotubes (Deal International or Strem Chemicals) was taken in a round-bottomed flask. Following the procedure of Green et al (16), 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 μ g 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.

TEM of functionalized CNT showed characteristic nanotubular 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.

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 Leibeig 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.

RESULTS AND DISCUSSION

To explore the catalysis of functionalized multiwalled CNTs, aniline oxidation is carried out with aniline/peroxide 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

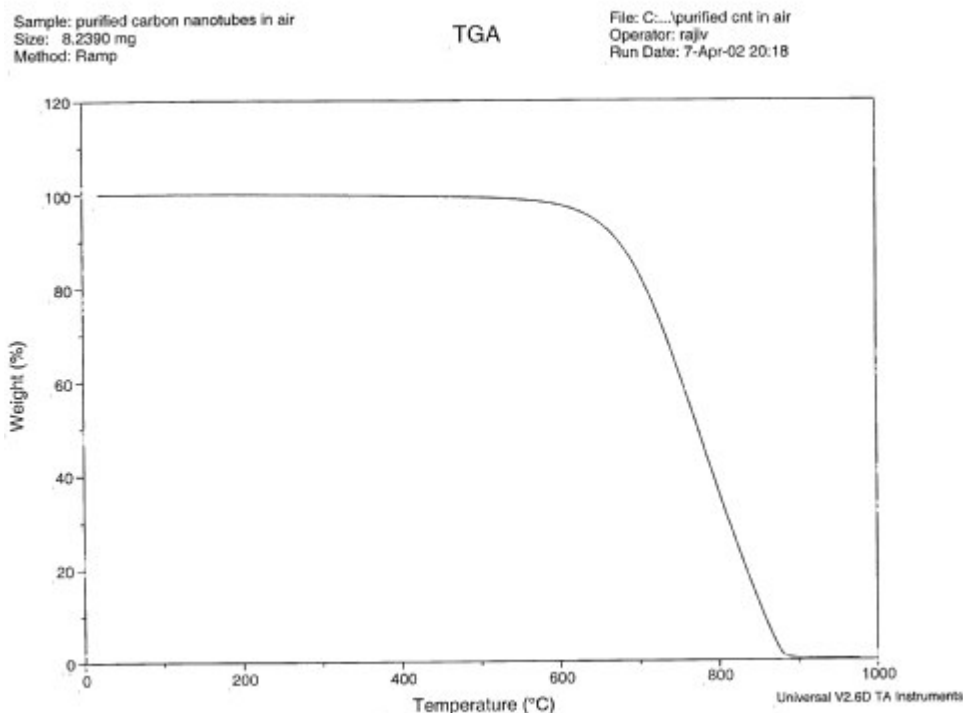


Fig1: Thermogravimetric analysis of functionalized multiwalled carbon Nanotubes

generating a reddish product diffusing into the solution. Note that the density of the multiwalled CNT is about 1.6-1.8 (24-26) 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

Coupling of Nitrosobenzene and Aniline

The first step in the oxidation process appears to be the formation of nitroso benzene (4-10) 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.

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 2 shows the magnitude of increase in optical density.

Extraction of Products from CNT

The products of the aniline oxidation remaining in the CNTs have been extracted into acetonitrile or acetone by sonication for about one hour. Upon examination of the extracted solution by UV-VIS spectroscopy, characteristic peaks at 327 and 425 nm are observed. 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.

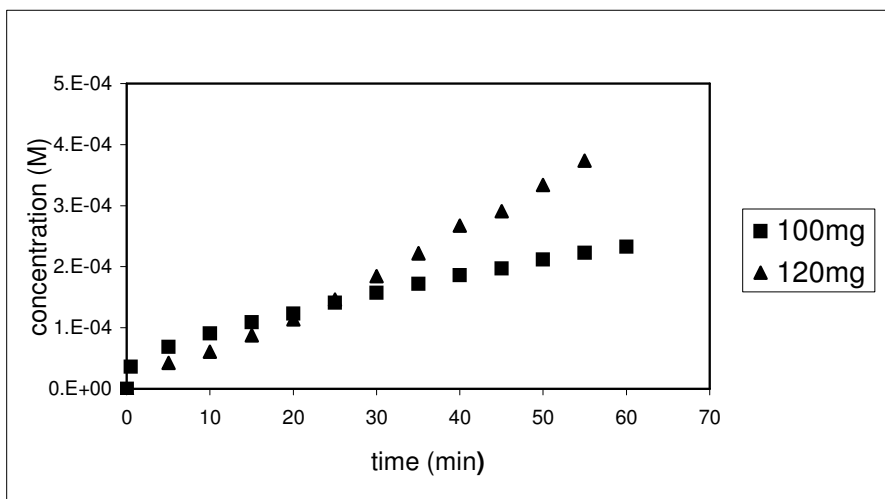
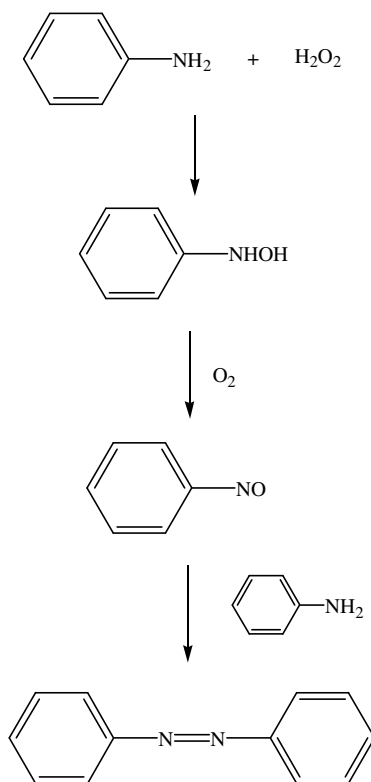


Fig 2: Concentration of azobenzene formed with different amounts of functionalized CNTs.

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 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.

ACKNOWLEDGEMENT

The authors thank Mr. N. Raravikar (RPI) for help in recording the TEM of the samples.

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