

Conversion of anilines to their oligomers by copper hexacyanoferrate(II)

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Aniline, *p*-toluidine and *p*-chloroaniline have been oxidized by copper hexacyanoferrate(II). The reaction was appreciable in basic medium. The resultant oxidation products deposited on copper hexacyanoferrate (II) surface are reddish brown in colour. The oxidation products have been characterized by GC-MS and IR spectroscopy. From the spectral studies, the oxidation product of aniline has been identified as tetramer, while that of *p*-toluidine and *p*-chloroaniline are trimer and dimer, respectively.

During the course of chemical evolution, cyanide ions were abundant in nature. Cyanide ion is smaller in size and is considered as a strong ligand due to the presence of triple bond. It shows basic, ambidentate characteristics and forms a variety of complexes with transition metal ions^{1,2}. Metal hexacyanoferrate(II) mostly insoluble in water, could have played an important role as adsorbent³⁻⁶ and ion exchanger^{7,8} in the course of chemical evolution.

Reactions between amines and clays have been studied by a number of workers⁹⁻¹¹. Hasegawa carried out spectroscopic studies on the coloured products obtained by the reaction of clays with amines^{12,13}. Apart from these studies, reports were available on the reaction with benzidine and anilines¹⁴⁻¹⁷. Studies on the interaction of aromatic amines with metal hexacyanoferrates(II) and its relevance in evolutionary context, can hardly be seen in literature. During the interaction studies of aromatic amines with copper hexacyanoferrate(II), it was observed that aniline, *p*-toluidine and *p*-chloroaniline react with copper hexacyanoferrate(II) and gave coloured products.

In this paper studies on the interaction of aniline, *p*-toluidine and *p*-chloroaniline with copper hexacyanoferrate(II) have been reported. A tentative mechanism involved in the formation of coloured products is also proposed.

Experimental Procedure

Preparation of copper hexacyanoferrate (II)—Copper hexacyanoferrate(II) was prepared by the following method reported by Kourim *et al.*⁷. In brief,

a solution of potassium ferrocyanide (167 mL, 0.1 M) was slowly added to the copper chloride solution (500 mL, 0.1 M) under stirring conditions. The reaction mixture was then heated at 60°C on a water bath for 2-3 h and allowed to stand for 24 h at room temperature. The precipitate obtained was filtered and washed thoroughly with distilled water and dried in an oven at 60°C. The dried product was ground and

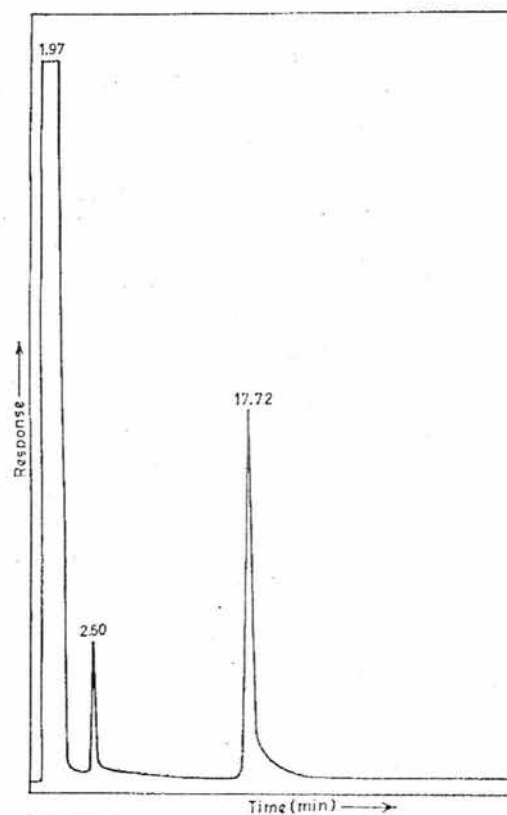


Fig. 1—Gas chromatogram of aniline products

*For correspondence

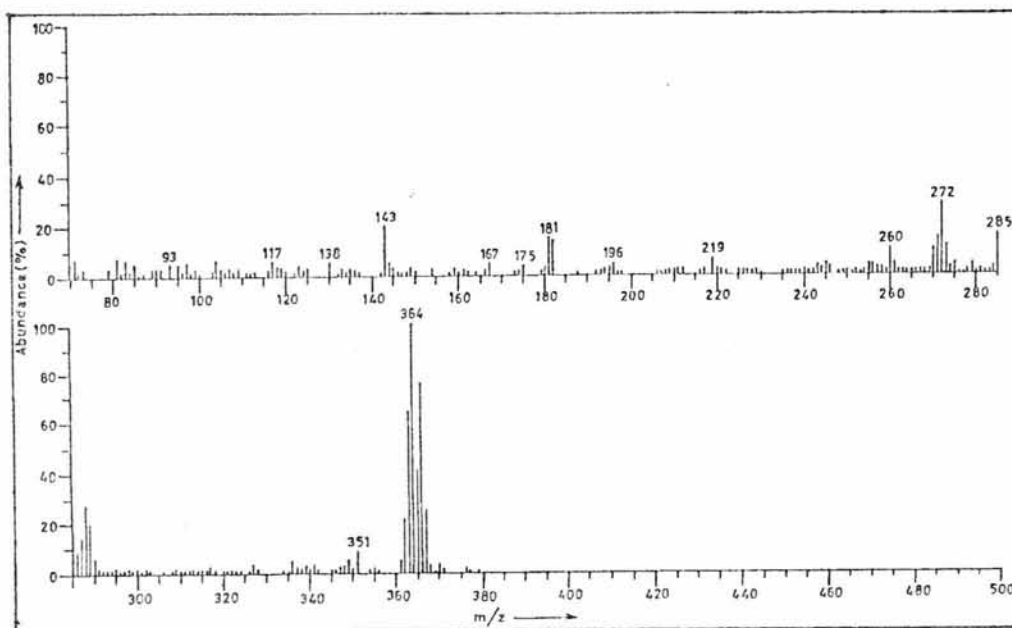
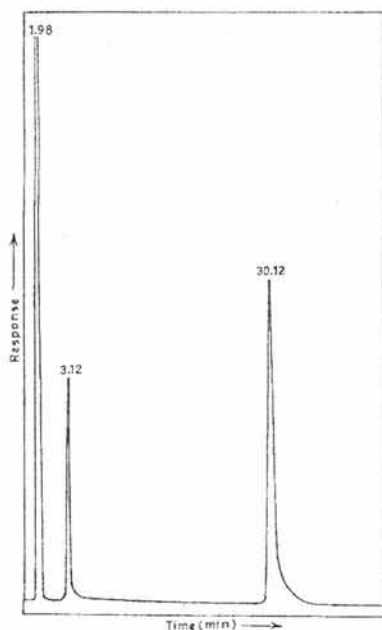


Fig. 2—Mass spectrum of aniline product

Fig. 3—Gas chromatogram of *p*-toluidine products

sieved to 100 mesh size. The purity of copper hexacyanoferrate(II) was checked by comparing X-ray data of the complex. The relative intensity data and interplanar spacing, d , were in good agreement with reported values¹⁸.

Oxidation of amines by copper hexacyanoferrate(II)—Oxidation of aniline, *p*-toluidine and *p*-chloroaniline was carried out by adding buffered amine solution (10 mL, 10^{-3} M) to 0.1

g of copper hexacyanoferrate(II) each time. The required alkaline *pH* 7-9, of the reaction medium is maintained using borax buffer. The suspensions were shaken using Expo Shaker initially for 1 h and then allowed to equilibrate with intermittent shaking at fixed time intervals. Reddish brown coloured products were deposited on the surface of copper hexacyanoferrate(II) within 72 h. These coloured products were extracted with the help of benzene. The coloured products soluble in benzene or acetone were separated with separating funnel and were concentrated for GC-MS and IR studies.

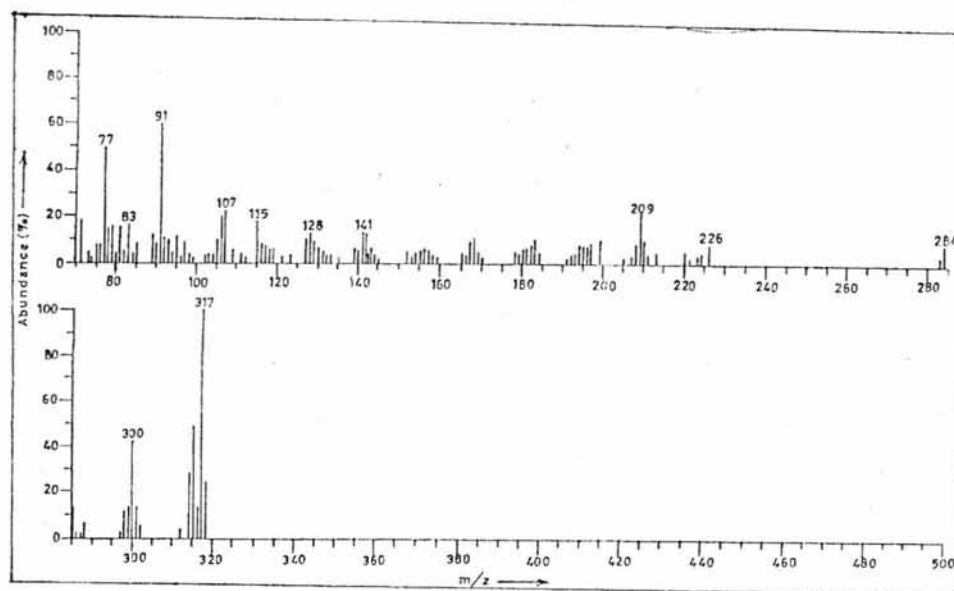
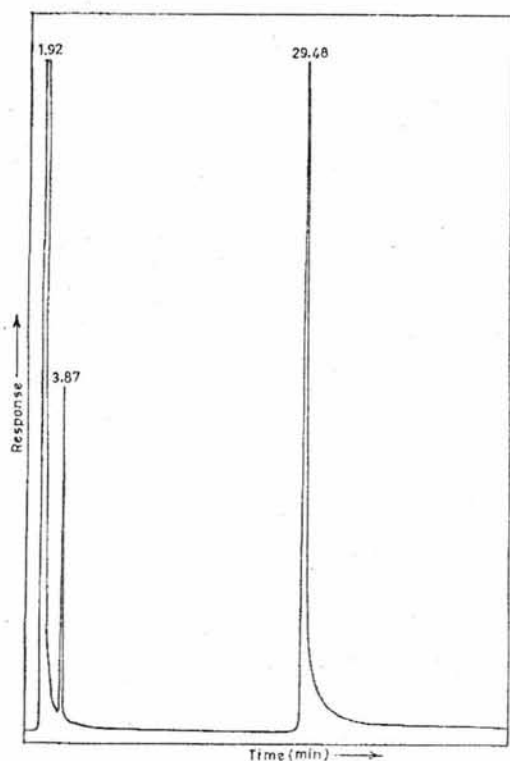
Surface area measurement—B.E.T. method was used to determine the surface area of copper hexacyanoferrate(II). In this technique, the surface area is determined by physical adsorption of N_2 at its boiling point. Value of surface area of copper hexacyanoferrate (II) is found to be $444.7 \text{ m}^2\text{g}^{-1}$.

Characterization—Analyses of the reaction products were performed on a Shimadzu gas chromatograph coupled directly to a Shimadzu QP - 2000 quadrupole mass spectrometer system.

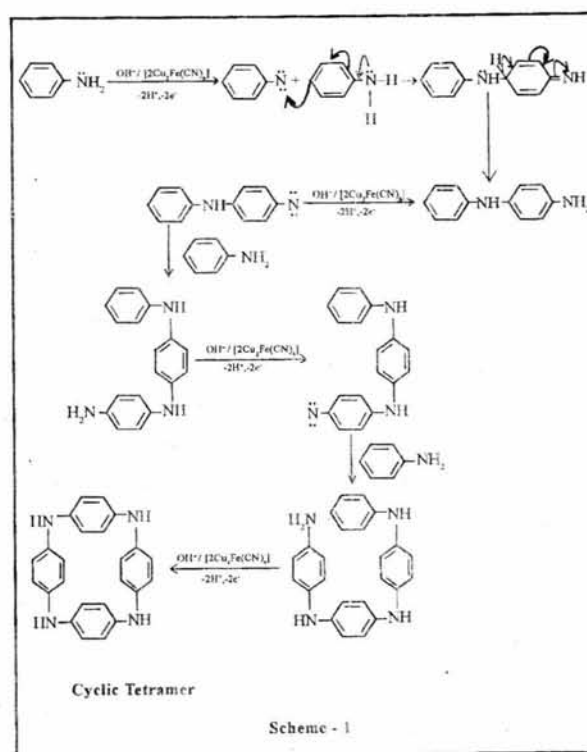
Infrared spectra of oxidation products have been recorded on KBr pellets using Perkin - Elmer FTIR series-1600 spectrophotometer.

Results and Discussion

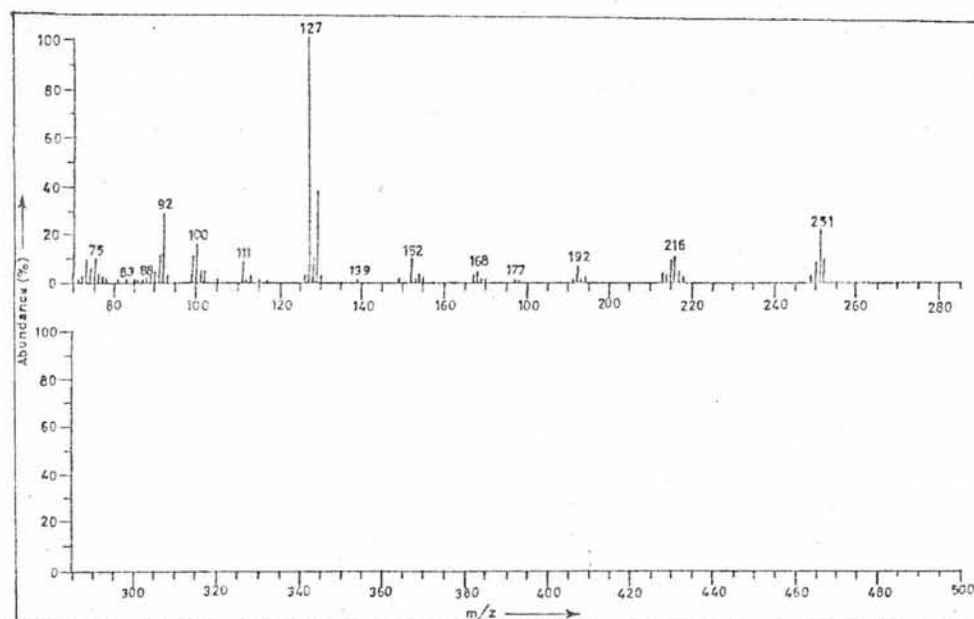
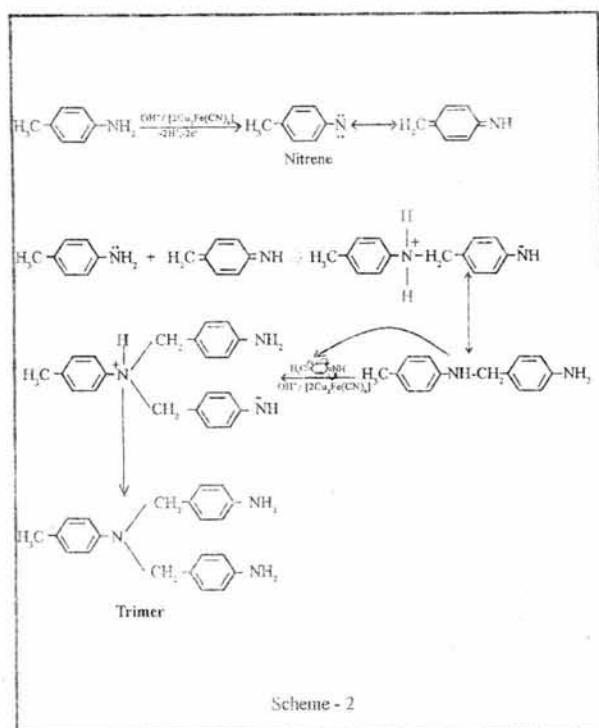
Several authors¹⁹⁻²² have shown that aromatic molecules give rise to oligomeric or polymeric compounds on clay surface. It may be reasonable to assume that anilines behave similarly on the surface

Fig. 4—Mass spectrum of *p*-toluidine productFig. 5—Gas chromatogram of *p*-chloroaniline products

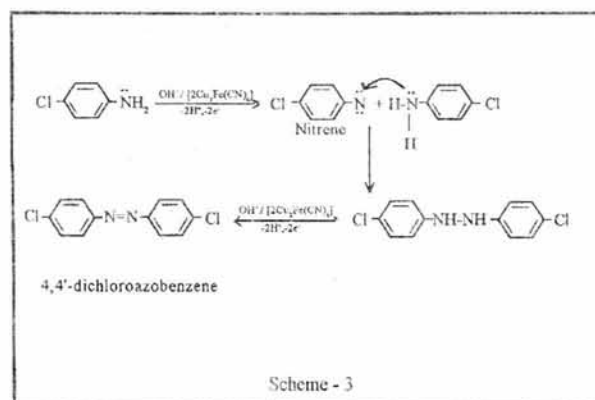
of metal hexacyanoferrate (II). Reactions of aniline, *p*-toluidine and *p*-chloroaniline with copper hexacyanoferrate (II) were studied over a wide pH range (7-9). It was found that reaction of all the three amines with copper hexacyanoferrate(II) was



appreciable only in alkaline medium ($pH \sim 8$). In acidic medium, no noticeable reaction took place. Further, the reaction when carried out in basic medium, the desired products were formed within 72 h, whereas it took about 30 days in case of neutral solution.

Fig. 6—Mass spectrum of *p*-chloroaniline product

Characterization—Fig. 1 shows chromatogram of aniline products, obtained by the reaction of copper hexacyanoferrate(II). Two peaks were found with retention times (R.T.) of 2.60 and 17.72 min. Peak with retention time 2.60 min was for starting material i.e. aniline, whereas, 17.72 min corresponds to main oxidation product. GC-MS analysis of the peak with



R.T. \approx 17.72 min showed a compound with molar mass $m/z \approx$ 364 (100%) and resembles to tetramer of aniline (Fig. 2). Some other high mass peaks observed in the fragmentation pattern were 351(8.4%), 285(15.4%), 272 (28.0%), 260(10.1%), 181(14.8%) and 93(4.7%). The observed masses are in accordance with the fragmentation pattern of proposed aniline tetramer by electron bombardment that takes place in the ion source of the mass spectrometer. No reaction product was found when alkaline buffered aniline solutions were kept without copper hexacyanoferrate(II) even after 240 h. This shows that anilines do not interact with buffer. From the infrared studies, single N-H stretching of medium intensity is observed at 3407 cm^{-1} . A band at 1516 cm^{-1} is due to the presence of δ N-H. Sharp band of aryl ν C-N is

found at 1363 cm^{-1} and a band around 827 cm^{-1} shows the *p*-substitution in benzene ring. On the basis of mass spectra and IR studies, the most probable structure and tentative mechanism²³ are proposed (Scheme-1).

Tetramer of aniline is formed through nitrene intermediate. Nitrene formation involved two-proton and two-electron transfer reaction. Cu(II) changes to Cu(I) state during the process which is also a stable state²⁴. Further, this electron deficient specie being attacked by another aniline molecule in the presence of OH⁻ ions give rise to a dimer and the process continues till the formation of a tetramer.

The oxidation product of *p*-toluidine gave two well defined and well separated peaks in gas chromatogram with R.T. of 3.12 and 30.12 min (Fig.3). Mass spectrum of the peak with R.T. at 30.12 min showed molar mass $m/z = 317(100\%)$, which corresponds to trimer of *p*-toluidine (Fig. 4). Some high mass fragments observed were 300(42%), 284(13.3%), 226(7.7%), 209(20.8%), 115(17.5%), 107 (21.7%), 91(59.5%) and at 77(49.1%). Above fragment masses resembled with possible fragments of a trimer. Peak with R.T. of 3.12 min corresponded to the starting material, i.e. *p*-toluidine.

IR spectrum of trimer showed a symmetric $\nu\text{N-H}$ bands at 3276 cm^{-1} and antisymmetric $\nu\text{N-H}$ at 3370 cm^{-1} indicating the presence of amine group. $\delta\text{N-H}$ band is found at 1621 cm^{-1} and $\nu\text{C-N}$ at 1360 cm^{-1} , C-H stretchings at 2928 and 2858 cm^{-1} are also seen in the spectrum. Band at 804 cm^{-1} shows that the *p*-substitution is a benzene ring. Tentative mechanism involved and possible structure of trimer product is shown in Scheme 2.

Reaction products of *p*-chloroaniline were separated on gas chromatograph (Fig. 5). Two major peaks were found in gas chromatogram. Peak with retention time 3.87 min corresponded to starting material i.e. *p*-chloroaniline, whereas, the second peak with retention time of 29.48 min corresponded to the main oxidation product. A clear peak on GC-MS corresponding to peak with retention time 29.48 min. showed molar mass $m/z = 251(24.2\%)$ for a dimer of *p*-chloroaniline (Fig. 6). Other fragmentation products of a dimer were observed at m/z 216(11.1%),

139(1.3%), 127(100%), 111(8.4%), 92(29.1%) and 75(10.3%).

Infrared spectrum of *p*-chloroaniline oxidation product showed a well defined and very sharp peaks at 1596, 1445, 1422 cm^{-1} due to -N=N- bond. Probable structure and tentative mechanism is given in Scheme 3.

Conclusions

It is observed that $\text{Cu}_2[\text{Fe}(\text{CN})_6]$ reacts with all the three anilines (aniline, *p*-toluidine and *p*-chloroaniline) to give a coloured product. Aniline was found to polymerize to a cyclic tetramer, whereas, *p*-toluidine and *p*-chloroaniline afforded their trimer and dimer, respectively. It is important to note that these reactions occurred only in alkaline medium at pH 7-9. Copper which is in its oxidation state (II) in $\text{Cu}_2[\text{Fe}(\text{CN})_6]$ possibly changes to another stable oxidation state²⁴ (I).

Acknowledgement

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