Pakistan J. Sci. Ind. Res., Vol. 30, No. 5, May 1987

CHARGE TRANSFER COMPLEX FORMATION BETWEEN SUBSTITUTED AROMATIC AND ALIPHATIC CARBONITRILES AND IODINE MONOCHLORIDE

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(Received December 22, 1986; revised February 17, 1987)

A study of molecular complexes of various aromatic and aliphatic carbonitriles was undertaken as a means of determining equilibrium constants. Such complex formation techniques have also been used as a means of comparing the mode of transmission of electronic effects of the substituents in aromatic alicyclic and open chain systems.

Key words: Aromatic and aliphatic carbonitrile, complex formation, charge transfer complexes.

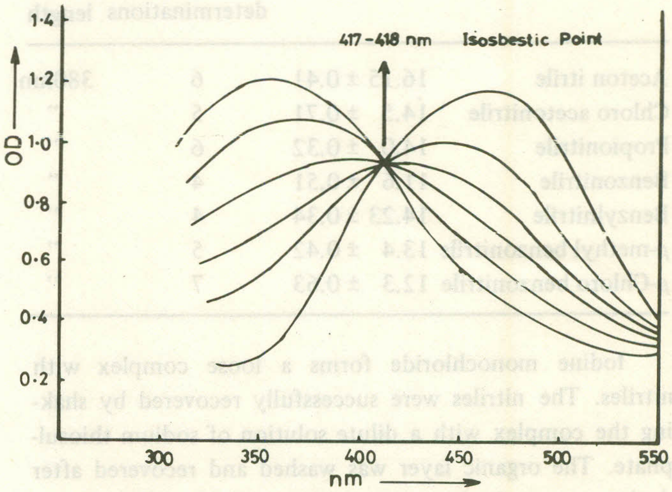
INTRODUCTION

It is known that certain compounds combine in 1:1 ratio to form additional products called molecular complexes, in which one component is an electron donor and the other is an acceptor.

$$A: + B \rightarrow A^{+} \text{------} B^{-}.$$

These are often designated as charge transfer complexes. Such complexes are often too weak to be isolated, but may be studied in solution. The existence of such complexes has been recognised by the study of physical properties, such as the change in colour by the addition of one compound to the other. Iodine has a violet colour in inert solvents such as carbon tetrachloride, whereas a red to brown colour in benzene or other aromatic solvents. According to Benesi and Hilderbreand [1] the behaviour of iodine was due to an acid-base interaction in the electron-donor and acceptor sense. Spectral studies of such complexes show pronounced changes in absorption spectra. The complexes of Iodine and aromatic hydrocarbons show absorption in the region 280-400 nm, a region where the violet solution of Iodine shows no absorption. The absorption peaks shift from longer wavelength, i.e. 400-700 nm to a shorter wavelength, i.e. 280-400 nm. A regular shift is observed with the increase in the number of methyl groups in the benzene ring [2]. The basicity of benzene ring increases with the introduction of methyl groups.

Similar studies have been reported by Andrew and Keefer [3]. They studied the molecular complexes of alkyl substituted benzene and Iodine monochloride. Klaboe [4] studied the complexes of iodine monochloride with benzonitrile and propionitrile. Here complex formation almost certainly occurs between the lone pairs of electrons of the -C ≡ N group and the halogens which accept the electrons.



Absorption spectrum of 4-Methylbenzonitrile-Iodine monochloride complexes

Here we describe the results of the study of the charge transfer complexes of certain aliphatic and aromatic nitriles. Complex formation seems to be quite susceptible to substituent effects, and our aim is to observe, measure and interpret the effect of remote substituents of both electron attracting and donating types.

RESULTS AND DISCUSSION

Measurements of the formation constant values were based on the methods used by Peter Klaboe [5]. Spectroscopic measurement were made on a Unicam SP-500 instrument (manual) and repeated on an SP-800 recording instrument. All measurements were done at room temperature 26° ± 0.5°.

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To determine the formation constants of the complexes of stoichiometry 1:1 a series of solutions were made in carbon tetrachloride. The concentration of iodine monochloride was kept constant and that of nitriles varied from 3.0×10^{-2}M to 6.0×10^{-1}M. All spectra were recorded within half an hour.

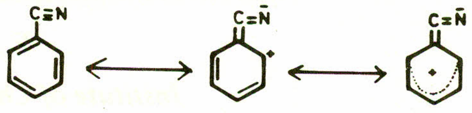
Iodine monochloride showed absorption in the region of the complex absorption. Therefore the first calculated K_c (formation constant) was on approximate value. The absorbence due to free Iodine monochloride was calculated and subtracted from the absorbence due to the complex. The calculations were repeated to get two constant values for K_c. Table 1 lists the K_c values of some of the compounds studied.

Table 1. Formation constant in carbon tetrachloride at $26^{\circ} \pm 0.5^{\circ}$ $R\text{-}C\equiv N + RC\equiv N \ldots\ldots Icl$

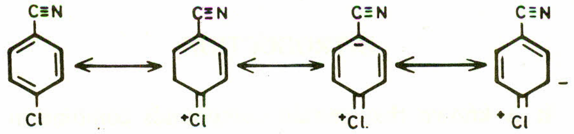
Compound	Kcl moles^{-1}	No. of separate determinations	wave length
Aceton itrile	16.15 ± 0.41	6	380nm
Chloro acetonitrile	14.5 ± 0.71	5	"
Propionitrile	14.0 ± 0.32	6	"
Benzonitrile	11.6 ± 0.51	4	"
Benzylnitrile	14.23 ± 0.34	4	"
p-methyl benzonitrile	13.4 ± 0.42	5	"
p-Chloro benzonitrile	12.3 ± 0.63	7	"

Iodine monochloride forms a loose complex with nitriles. The nitriles were successfully recovered by shaking the complex with a dilute solution of sodium thiosulphate. The organic layer was washed and recovered after drying over anhydrous magnesium sulphate. The purity of the nitriles were checked by V.P.C.

The K_c value for acetonitrile is higher than that of chloroacetonitrile. This is quite up to our expectations. The inductive effect of chlorine makes the electrons less available on the cyano group, and hence retards the complex formation, whereas proionitrile has a K_c value higher than that of acetonitrile. Therefore in aliphalic compounds it appears that complex formation is sensitive to electronic effects. In aromatic series the K_c value of benzonitrile is lower than that of benzylnitrile. This probably is because of the resonance involvement of the ring electrons with the -CN group:



Whereas in benzylnitrile both ring electrons as well as the electrons of -C = N group participate in complex formation. The K_c value of chlorobenzonitrile is higher than that of benzonitrile. This could be interpreted in view of the mesomeric effect of chloro group being more important than its inductive effect.



p-Nitrobenzyl nitrile showed no or a very little solubility in carbon tetrachloride. *p*-Amino benzonitrile underwent a substitution reaction on the ring. The two substituents mentioned above could give interesting results because of strong and opposite electronic effects.

From our above reported results we conclude that loose complex formation is equally sensitive to electronic effects as any other chemical reaction would be. The mode of the transmission of substituents effects can be carried out similarly on alicyclic compounds. It can also prove to be a good technique for studying such an effect in a system where aromatic and alicyclic systems are centred on a common carbon.

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