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SPECTROSCOPIC AND CONDUCTIVE PROPERTIES OF SOME CHARGE TRANSFER COMPLEXES OF IODINE

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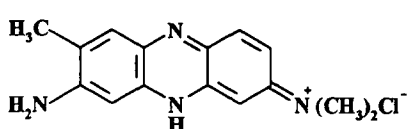
Abstract

The interaction of iodine with donor bases such as neutral red (NR) and 1,10 - phenanthroline (Ph) have been studied spectrophotometrically in C_2H_5OH . The results indicate the formation of 2:3 charge transfer complexes of the type $(base)_2I_2$. Mass, Raman and 1H NMR spectra have been recorded for each complex. I_3^- and I_2 species are observed in these complexes. In addition, the d.c. conductivity is measured in the range (300-400) K° . The energy gap of the ionic conduction has been calculated. The conduction process is thought to involve iodide transfer between polyanions.

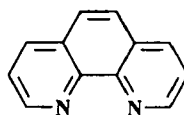
Introduction

Polyiodides have a considerable interest and a high importance in recent years (1-5) Since some solid complexes exhibit an interesting physical properties such as electrical conductivity (6-7). Substances with metal-like conductors have been synthesized and these compounds are reported to contain ions such as I_3^- and I_5^- . These polyiodides form a remarkable group of salts of MI_n type, where M is one of the larger alkali metal ions, a substituted ammonium ion or an arsonium, phosphonium ion or organic cation such as N- alky acridinium (8-12) and $n=3,4,5,7$ or 9 . In the triiodide crystals of a known structure, the triiodide anions exist as separated individuals. In the higher polyiodides, the anion assembly is made up of a number of sub-units (I^- , I_3^- and I_2 molecules) which are loosely held together to form more complex I_n system. The

electrical conductivity of the polyiodides was of the order $10^{-5} - 10^{-12} \text{ S cm}^{-1}$ and had close connection with the number of iodine atoms of the polyiodide anion (12). The size of the cation increases the deformation of the iodine framework and as expected influences the electrical properties of the corresponding complexes. Therefore, iodine framework in the crystal structure is of primary importance in the determination of conductivity of polyiodides. In this work the prepared polyiodides of neutral red (I) and 1,10-phenanthroline (II) form a structure analogous to that of pyridine and acridine complexes (13-14). The aim of this work is to characterize the reaction products and to study the nature of the iodine molecules complexed in these reactions. The spectroscopic analysis demonstrated that the added iodine is incorporated into polyiodide species. Electrical measurements also, indicate that both ionic and electronic conduction are present in the polyiodide complexes.



(I)



(II)

Results and Discussion

Electronic Spectra

The electronic spectra of the iodine complexes show a new absorption band in $\text{C}_2\text{H}_5\text{OH}$ near 360 nm. It appears to be of the electron donor-acceptor type:

$n(\text{base}) \longrightarrow \sigma^*(\text{I}_2)$. The composition of the complexes mentioned above has been confirmed, in solution according to the known methods (15) and is shown in Figure 1.

This result is in agreement with the elemental analysis of the isolated solid complexes and their mass spectra.

Mass Spectra

The spectra indicate that the molecular ion of $(\text{NR}-\text{I}_2)$ complex is stable and is equivalent to 1339.8 and that of $(\text{Ph}-\text{I}_2)$ complex is unstable and is equivalent to 1122.0. The base peak in the latter complex is corresponding to $\text{C}_{12}\text{H}_6\text{N}_2\text{I}_2$.

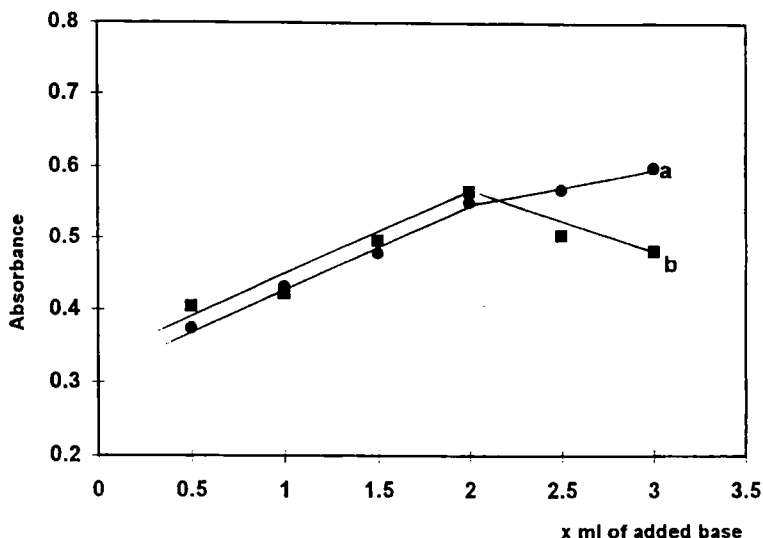


Figure 1. Photometric curve of (a) (NR- I₂) complex and (b) (Ph- I₂) complex in ethanol.

The graphs indicate that the formed iodine complexes consist of two moles of the base and three moles of I₂, i.e the complexes should be formulated as (base)₂ (I₂)₃.

Raman Spectra

The Raman spectra of the two iodine complexes are shown in Figure 2 and the observed frequencies are summarized in Table 1. The spectra observed are just what would be expected for a mixture of I₃⁻ and I₂ species and not I₅⁻ unit. The I₂ stretching mode is observed as an intense Raman band at 180 cm⁻¹ in the two complexes studied and two bands around 105 and 155 cm⁻¹ for (NR-I₂) complex and at 115 and 150 cm⁻¹ for (Ph-I₂) complex. In both complexes the first band (105-115 cm⁻¹) can be assigned to the symmetric I-I stretch, ν_s (I-I) of the triiodide, whereas the second band (150-155 cm⁻¹) can be assigned to the asymmetric I-I stretch of I₃⁻, ν_{as} (I-I). These assignments agree quite well with those reported for many complexes (3,16). The exact nature of the cation in these complexes is still not clear (17) However, the 2 : 3 base: I₂ ratio known for these reactions may suggest that the cations are of the type

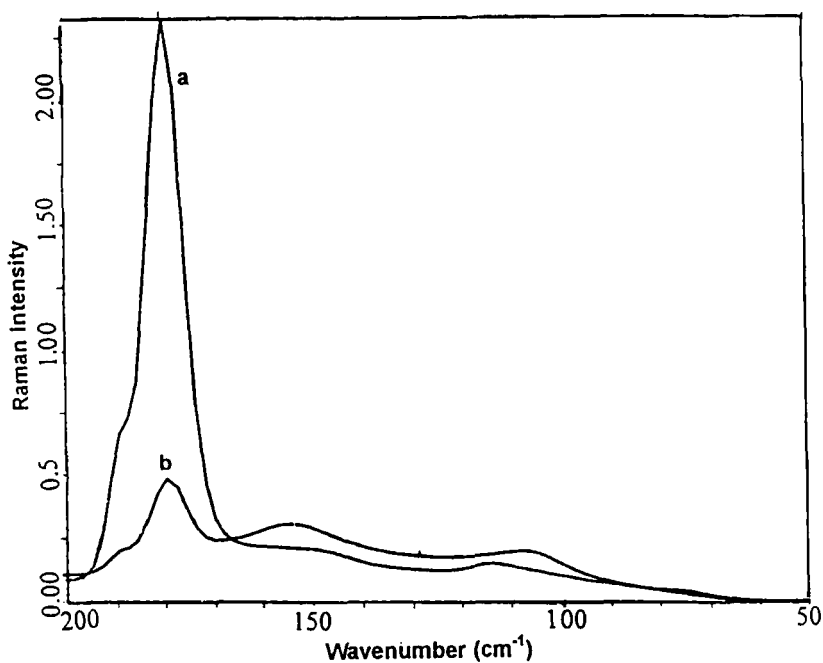


Figure 2. Raman spectra of (a) (NR-I₂) complex and (b) (Ph-I₂) complex.

Table I. Raman frequencies* cm⁻¹ for (NR)₂I⁺₃⁻I₂ and (Ph)₂I⁺₃⁻I₂ complexes.

(NR) ₂ I ⁺ ₃ ⁻ I ₂	(Ph) ₂ I ⁺ ₃ ⁻ I ₂	Assignments
105 m	115 m	ν _s (I-I)
155 m	150 w	ν _{as} (I-I)
180 v.s	180 s	ν (I ₂)

*s = strong, m = medium, w = weak, v = very

$(\text{base})_2\text{I}^+$ analogous to the $(\text{Ac})_2\text{I}^+$ and $(\text{HMTA})\text{I}^+$ described by Bowmaker and co-workers(2,14). Therefore, the complexes are formulated as $(\text{NR})_2\text{I}^+\text{I}_3^-$ and $(\text{Ph})_2\text{I}^+\text{I}_3^-$.

NMR Spectra

^1H NMR spectrum for neutral red revealed signal at 2.3 which is assigned for CH_3 group and two singlets at 3.17 and 3.43, assigned for two N- methyl groups. The spectrum also, revealed two signals at 6.71 and 6.88 which are assigned for NH_2 and NH protons, respectively. The aromatic protons show two groups of signals, the first lies in the range 7.63 - 7.76 and the second at 7.32 - 7.37. In the iodine complex all signals are more downfield shifted and appeared at 2.5, 7.33, 7.36, 7.75 and 7.78, respectively. A multiplet groups also, appeared in the range 7.87-7.92 and 8.02-8.07. ^1H NMR spectrum for 1,15 Phenanthroline showed signals at 7.74, 7.80 . 7.98 beside a multiplet at 8.46- 8.51 and 9.11- 9.13 which are assigned to the aromatic protons. In the iodine complex the signals are downfield shifted and appeared at 8.02 - 8.09, 8.23, 8.83 - 8.87 and 9.23 -9.25, respectively. This shift is due to the ring current influence of the magnetic anisotropy of nitrogen atoms and the field effect of the electronic dipoles located on the nitrogen atoms.

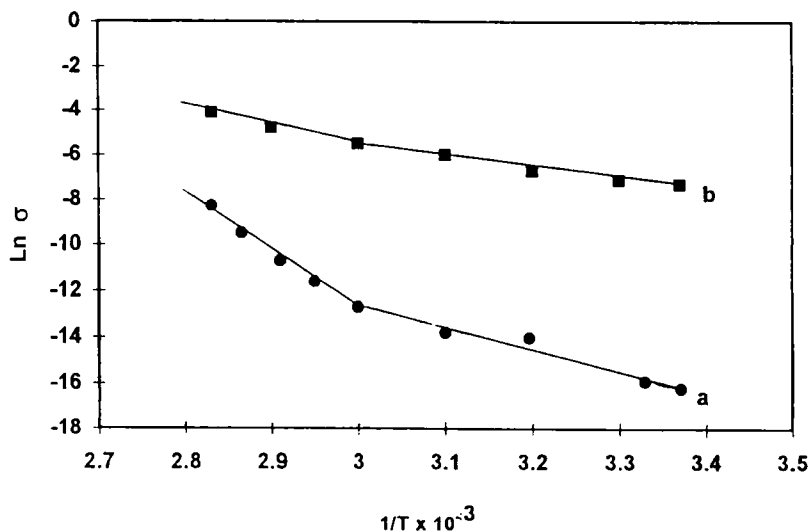
Conductivity Measurements.

The variation in the conductivity with temperature was found to obey the usual equation of electrical conduction (18) $\sigma = \sigma_0 e^{-E_g/2KT}$ where, E_g is the activation energy for conduction, σ_0 is the conductivity at infinite temperature and the other terms have their usual meaning. The electrical conductivity data (E_g , $\ln\sigma_0$) are collected in Table 2. It may be seen in Figure3. that the plot of logarithm of conductivity versus reciprocal temperature gives two straight lines with a break. The activation energy for the upper part of the break is smaller than that for the lower part in the two complexes studied as it increases with increase in temperature.

The activation energy for the two complexes is higher than that previously reported (19) for solid iodine (1.24- 1.30 eV). It may be expected that the fundamental process of the conduction will be the same in both polyiodide and solid iodine. The activation energy for the conductivity along the iodine net is considered to be

Table 2 . Electrical conductivity data for the complexes studied.

Sample	E_g	$\ln \sigma_0$
(NR - iodine) complex	1.62	24
	4.38	96
(Ph - iodine) complex	1.87	11
	3.30	22

Figure 3. d.c. Electrical conductivity $1000 / T$ relation for (a) NR ; (b) Ph complexes.

determined by the shortest distance between polyiodide ion such as in the case of crystalline iodine (9). Gileadi et al (20) . have examined equivalent conductivity and transference number of R_4NBr in Br_2 -containing solutions and implicated an ion hopping mechanism involving a polybromide species when Br_2 exceeds 1M. A similar mechanism has also been suggested to account for conduction in iodine (6,21,22). The high concentrations of iodine in these complexes along with the stability of polyiodides likely candidates for an ion hopping mechanism involving iodide transfer between polyiodides .

Experimental

The neutral red and 1.10 - phenanthroline were of BDH reagent grade , while reagent grade quality iodine was used without further purification . The same method of preparation was applied to obtain each of the two iodine complexes which is described as follows: An ethanolic solution of iodine (2×10^{-3} M) was added to a solution of the base in ethanol (1×10^{-3} M), stirring continuously. (NR.I₂) complex was separated immediately as a fine black crystals, while (Ph-I₂) complex was left over night for precipitation as a greenish black ppt. The two complexes were washed with a minimum amount of ethanol, dried and characterized by elemental analysis. (NR-I₂) complex was calculated as C₃₀H₃₄N₈Cl₂I₆ [Found: C, 25.4 (26.7); H, 3.00 (2.54); N, 7.70 (8.37) and (Ph-I₂) complex as C₂₄H₁₆N₄I₆ [Found: C, 26.4 (25.67); H, 1.90(1.43); N, 4.80(4.99). The calculated values are showed in parantheses.

Spectroscopic Measurements

The electronic absorption spectra of the complexes in ethanol were recorded using Shimadzu UV - 1601 PC, Photometer, Kyoto, Japan. The reaction between iodine and each of the nitrogen base (NR) nd (Ph) were studied spectrophotometrically in C₂H₅OH. The concentrations of iodine were kept constant at 1.20×10^{-4} and 1.50×10^{-4} M, respectively. While the concentrations of bases were varied over the range 0.20×10^{-4} to 1.20×10^{-4} and 0.25×10^{-4} to 1.50×10^{-4} M, respectively. These concentrations produce base: I₂ ratios from 0.5:3 up to 3:3. Mass spectra were measured with Mass Spectrometry Service Finnigan SSQ 700 . Raman spectra were recorded on Raman Spectrometer Bruker TRA 106 S 66 using ND Yag laser. Varian Gemini 200 (200 MHz ¹HNMR) Spectrometer was used to record the NMR spectra of the samples in DMSO. For d.c. conductivity measurements the powder complexes were pressed into 0.2 - 0.3 cm disk . Good contact was achieved through two coaxial carbon-dag electrodes applied to the two parallel faces of the sample. The area of each electrode was about 1 cm³ covers approximately half of the sample area . A thin copper wire was fixed to each electrode by silver-dag. The d.c. conductivity was measured under controlled equilibrium conditions in the temperature range 25° up to about 120°C. The conductivity of the sample (σ) was obtained using the general

formula $\sigma = I/V \cdot d/a$, where I is the current in ampere . V is the potential drop across the sample of cross section area " a " in cm^2 and thickness d in cm .

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