Studies on the Molecular Complexes of Para-Benzoquinone and Aminoacids. Part II

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Solid compounds of para-benzoquinone (PBQ) with amino acids (glycine, alanine, methionine and arginine) were prepared. Analysis of the data confirms that the composition of the compounds formed between PBQ and aminoacids are generally in the ratio 1 : 2. Efforts have been made to explore the nature of the compounds. The compounds are diamagnetic in character. Solid compounds show marked semiconducting properties, the energy of activation being in the range of 0.80-1.15 ev,

A number of complexes have been reported from the interactions of quinones with aminoacids[1-8]. But controversy exists as to the nature and composition of the complexes whether they are electron-donor acceptor (EDA) complexes or addition reactions[3].

In order to understand the nature of the complexes formed between p-benzoquinone and aminoacids, it is desirable to isolate the solid compounds if possible and determine their structure.

Further, studies of amino-quinone[4-8] complexes have indicated that these materials in the solid state have electrical conductivities which are higher than those of the components by 6 to 12 orders of magnitude. It is natural to expect that the aminoacid-quinone compounds may have electrical conductivities and the aspect is worth studying. These studies might provide insight into some of the energy transfer and storage mechanism in biological systems.

We present in this communication the preparation and purification of the solid compounds of p-benzoquinone (PBQ) with aminoacids (glycine, alanine, arginine and methionine). Studies on the semiconducting properties of these compounds have also been presented.

Experimental

Purified aminoacid (glycine, alanine, arginine and methionine) in water was added to PBQ in ethanol (appreciably in excess of the stoichiometric amounts). The solution was heated to about 50° and kept for about 50 hours. The solution containing the coloured substance was evaporated under reduced pressure at low temperatures. The compound formed together with large amounts of PBQ and little aminoacid (if any) was repeatedly washed with ether (where only PBQ is soluble) and then with alcohol to remove traces of PBQ and aminoacid (the compound being more soluble in water

than alcohol). The compound was then dissolved, dried in vacuum and kept in a desiccator.

The compounds are highly hygroscopic even under ordinary conditions. The elemental analysis of the compounds are given to Table 1.

TABLE 1—ELEMENTAL ANALYSIS OF THE SOLID COMPOUNDS

Compound and m. pt.	Composition	Structure X	Structure Y	Y + 2H₂O	Found %
PBQ-Glycine	1 : 2	C 47.24	54.05	46.51	47.43
m. pt.		H 3.94	4.50	5.43	4.52
(254-255°)		N 11.02	12.01	10.85	11.05
		O 37.80	28.84	37.21	37.00
PBQ-Alanine	1 : 2	C 51.06	57.60	50.35	49.92
m. pt.		H 4.96	5.60	6.30	5.64
(285-286°)		N 9.93	10.20	9.79	10.32
		O 34.25	25.60	33.56	34.12
PBQ-Methionine	1 : 2	C 47.09	51.33	46.83	47.28
m. pt.		H 6.40	6.95	7.97	7.01
(218-219°)		N 6.90	7.49	6.83	6.91
		O 23.85	17.12	23.36	23.58
		S 15.76	17.11	15.61	15.22
PBQ-Arginine	1 : 1	C 52.38	55.93	91.97	51.10
m. pt.		H 5.56	5.93	6.30	6.30
(234-235°)		N 16.66	17.79	16.54	17.03
		O 25.40	20.45	25.19	25.59

Semiconducting Properties

We could not prepare the single crystals of the solid complexes. The powdered samples were, therefore, placed under the circular jig at pressure of 5 tons/cm². The diameters and widths of the tablets were measured by a microscope. Due to hygroscopic nature of the samples, the samples were protected from moisture by placing them in a tube containing fused calcium chloride even during the measurement of conductivity (Fig. 1).

The establishment of good, stable reproducible electrical contacts between the electrodes and the
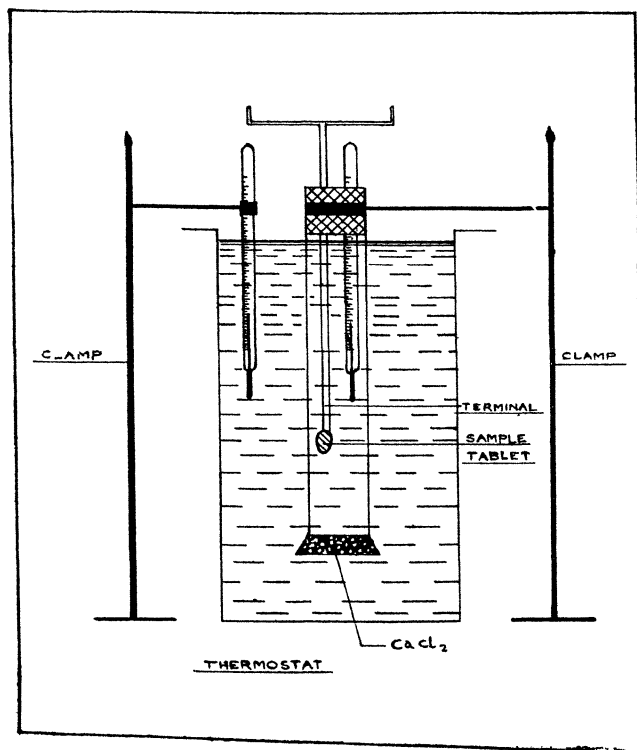
Fig. 1

Fig. 2

tablet proved to be difficult. After suitable metallic contacts (with Cu) had been made, the steady increasing voltage from a battery was applied across the samples and the resulting current flow was measured directly in a nanometer. The experiment was repeated at different temperatures. From the V-1 characteristic curves at different temperatures (a typical V-I characteristic curve for alanine-PBQ compound is given in Fig. 2) the resistances (R) and hence the resistivities (ρ) at different temperatures were calculated from the relation

$$R = \rho \frac{\text{length}}{\text{area}}$$

The results are given in Table 2.
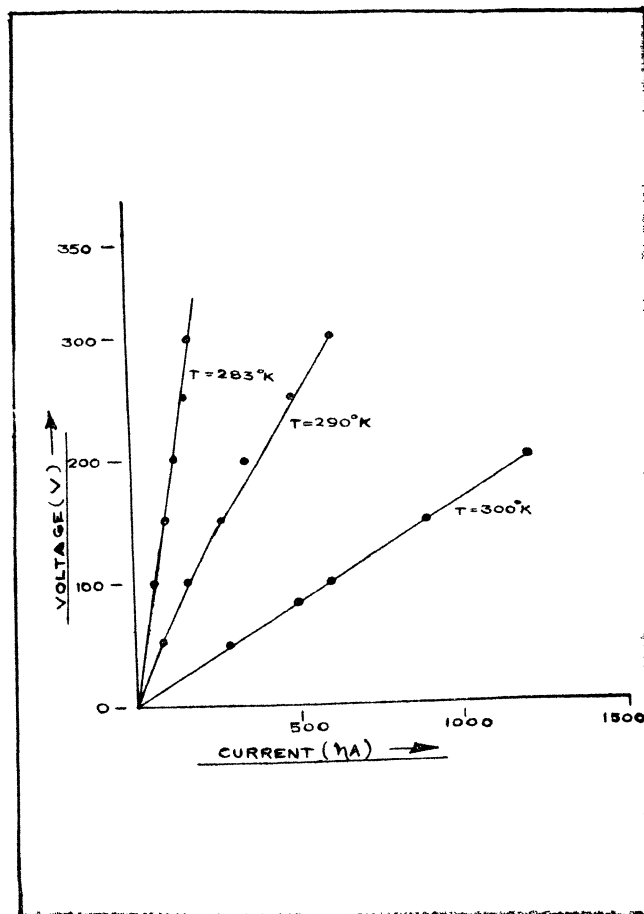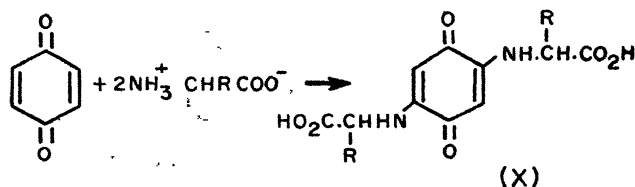
A typical plot of the specific resistivity versus the reciprocal of the absolute temperature for the alanine-PBQ compound is shown in the Figure 3. The activation energies are given in the Table 2.

Results and Discussion

The nature of the compounds, though interesting is yet not known definitely.

From i.r. studies, Slifkin[1,9,10] infers the compounds to be 1 : 1 C.T. complexes whereas the addition compounds (X) of the-type

have been suggested by Foster[3] similar to the observations made by Woker and Antener[11], Loffe and

. TABLE 2—DETERMINATION OF ACTIVATION ENERGY (E)

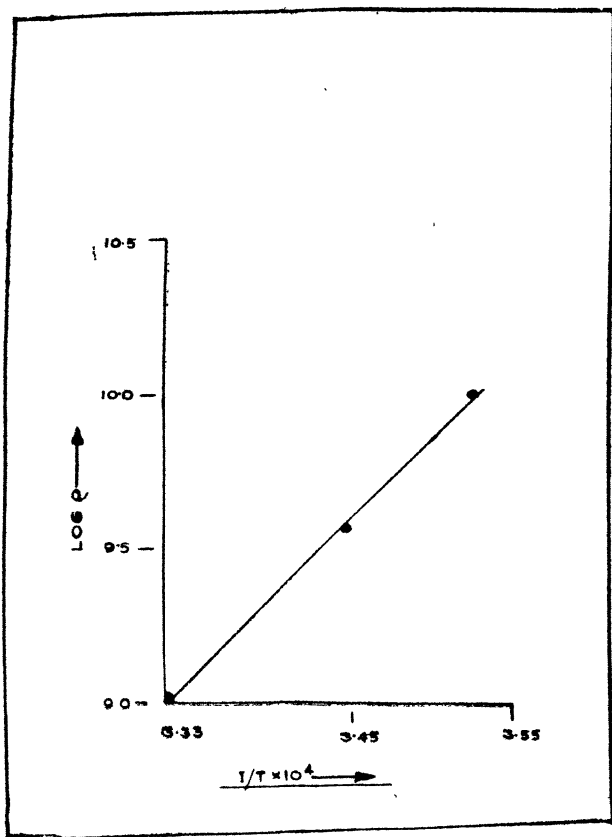| Compound	Temperature °K	Specific Resistance (ρ) ohm cm^{-1}	Activation Energy E(ev)
PBQ-Glycine	283	2.52×10^9	
	290	1.21×10^9	0.80
	300	3.93×10^8	
PBQ Alanine	283	9.77×10^9	
	290	3.57×10^9	0.95
	300	1.00×10^9	
PBQ-Methionine	283	6.49×10^9	
	290	3.05×10^9	1.05
	300	5.13×10^9	
PBQ-Arginine	283	4.44×10^9	
	290	1.61×10^9	1.14
	300	3.00×10^8	

Fig. 3

Khavin[12] and Michalek and Szarkowaka[13]. The structure has been reported to be confirmed by the isolation, purification and identification of (alanine +chloranil) compound from i.r. and n.m.r. studies[3]. From i.r. and polarographic studies, Chattopadhyay et al[14] report 1 : 1 C.T. complexes of the type
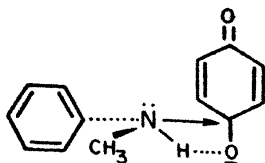
between PBQ and methylaniline (aniline, o-toluidine etc.).

We[15] however, believe that the reaction is
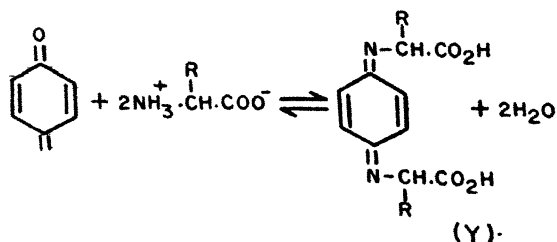
similar to Schiff's base type of reaction.

We have isolated and purified the solid compounds from quinone and aminoacids and the analytical data are reported in Table 1. From the results, it is very difficult to suggest which of the structure X or Y is correct. It is seen that the compositions of X and the compositions of $Y + H_2O$ are almost identical. I.R. studies are unable to help us much in this respect. We are unable to adduce further evidence from n.m.r. or mass spectral studies.

The hygroscopic nature of the products, water solubility lead us to believe that the nature of the product is Y rather than X.

All the compounds are diamagnetic in character as observed from magnetic moment measurements but the temperature dependence of magnetic moments could not be measured.

In determining the activation energies of the solid complexes, the equation

$$\rho = \rho_0 e^{-E_a/2RT}$$

used for the intrinsic semiconductors was not applied. Rather, we used the equation

$$\rho = \rho_0 e^{-E_a/RT}$$

as used by Tollin et al[8] following the suggestion of Fox[16], where E_a being the activation energy which can be regarded to be the difference between the highest point in the valence band and the lowest point in the conduction band.

The activation energy of the compounds lies between 0.87 ev to about 1.1 ev. The values are close to the values of the activation energies of molecular complexes of flavins and phenols. But the values are considerably higher compared with activation energies which have been obtained in other systems, e.g. 0.019 ev in pyrelene-iodine and 0.15-0.65 ev in the amine-quinone complexes[8].

It is to be noted in this connection that the results are qualitative rather than quantitative as

(a) The protons derived from presence of water of hydration in the solid complex may contribute to the conductivity[17].

(b) The use of powdered sample under high pressure changes the physical state of the samples so as to vitiate the results due to intergranular capacitance and resistance[17,18].

Inspite of the limitations, the conductivity changes can be explained by the removal of the electron from the donor to the acceptor leaving behind a 'hole' into which other electrons may flow similar to the observations of the amino-quinone

complexes in which the 'holes' carry the majority of the current.

It is not known definitely how far these electron-transfer processes are important in biological systems but surely such results can give much insight regarding the electron-transport mechanisms.

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