976. *Electron-donor and -acceptor Complexes with Aromatic Systems. Part VIII.*[1] *Preparations and Physical Measurements of New Metal Addition Complexes with Aromatic Systems in the Solid State.*

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The electrical properties of metal–aromatic complexes ArM_m in the solid state can be extremely sensitive to contamination by oxygen, moisture, or carbon dioxide. Methods of preparation of such complexes are detailed which ensure their complete protection from the atmosphere.

As one example, tetracyclic aromatic molecules are described which are sufficiently soluble in low-boiling ether solvents to allow preparation of complexes by ultrasonic activation of their solutions in contact with the free metal. Larger aromatic systems, for example, those with 9 fused rings, are not sufficiently soluble to permit this. Since the vapour pressure of the latter at ~400° is low, the complexes can be formed by diffusion of the metal vapour into the polycrystalline aromatic solid. This procedure is described for preparations of sodium and potassium complexes with isoviolanthrene.

Operations involving transfer into measurement cells or into weighing bottles have to be carried out in an inert atmosphere. A glove box for this purpose is described which incorporates a sodium-arc purifier to scavenge any atmospheric gases diffusing through the gloves.

Cells for measuring conductivity and thermoelectric power suitable for use in such a box are also illustrated.

PREVIOUS methods [2,3] of preparation of addition complexes of aromatic hydrocarbons with alkali metals have often relied on refluxing or stirring a solution of the organic compound in dry ether or another solvent, in contact with the free metal. This operation can require several days to afford complexes with a high content of metal atoms. During this time traces of oxygen or moisture can diffuse into the reaction solution to an appreciable extent, even when the solution is protected by nitrogen. Resulting products of oxidation may be sufficient to modify the electrical properties of the solid complex. Slough and Ubbelohde [4] gave a preliminary description of a method using ultrasonic activation of the solution to accelerate complex formation by the benzoquinolines in ethereal solvents. This method has now been extended, with a number of improvements, to the preparation of sodium complexes of the tetracyclic molecules, naphthacene, 1,2-benzanthracene, and 2,3-, 3,4-, and 1,2-benzacridine.

Molecules with more fused rings are, however, only slightly soluble in ethers with a low C : O ratio,[3] and this limits the usefulness of ultrasonic methods of preparation. Such molecules have high melting points and high sublimation temperatures, which facilitates the formation of their alkali-metal addition complexes by diffusion of the metal vapour into the solid at 400—450° in a high-vacuum system. Sodium and potassium complexes of isoviolanthrene have been prepared by this means.[5]

EXPERIMENTAL

Nitrogen (B.O.C. " White Spot "; $O_2 < 10$ p.p.m.) was purified from oxygen by passage (about 100 c.c./min.) through a column, 3 cm. in diameter and 200 cm. in length, containing copper turnings freshly reduced in hydrogen at 500°. The column was maintained at 490—510° along its length. The issuing gas was then freed from water vapour by passage through

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[1] Part VII, Martin and Ubbelohde, preceding paper.

[2] Holmes-Walker and Ubbelohde, *J.*, 1954, 720.

[3] Scott, Walker, and Hansley, *J. Amer. Chem. Soc.*, 1936, **58**, 2442.

[4] Slough and Ubbelohde, *J.*, 1957, 918.

[5] Parkyns and Ubbelohde, *J.*, 1961, 2110.

100% sulphuric acid, baked-out soda lime, and two traps packed with glass wool and cooled in liquid air.

Subsequent references to " nitrogen " refer to gas treated in this way.

Purification of Materials.—The aromatic tetracyclic hydrocarbons or bases were purified by the procedure as described in the previous paper. Isoviolanthrene is chemically less stable and was purified by the procedure adopted by Parkyns and Ubbelohde.[6] Dioxan, used in the preparation of the alkali-metal complexes of the tetracyclic aromatic systems, was refluxed with sodium until the metal remained bright, and twice distilled from bright sodium against a counter-current of nitrogen; the distillate was kept under nitrogen; it was pale blue, probably owing to dissolved sodium.[7]

Preparation in Ether-type Solutions.—Solutions of the tetracyclic aromatic hydrocarbons and bases reacted with sodium on ultrasonic activation. The ultrasonic probe and reaction cell are shown in Fig. 1. The purified hydrocarbon (0·5 g.) was added to the cell which was kept protected by a stream of nitrogen; purging with nitrogen was continued for a further half-hour. Dioxan (15 ml.) was distilled into the vessel against the flow of nitrogen and a " pea " of bright sodium (kept in purified dioxan under nitrogen) was then added to the vessel. The colour of the aromatic mononegative ion appeared immediately on the surface of the sodium. The ultrasonic probe was then inserted slowly against the counter-flow of nitrogen and was fixed at the nodal position by a Neoprene gasket (C) which provided a gas-tight seal to the Pyrex-glass reaction vessel. The probe was vibrated by means of a transducer head (A) brazed to the stainless-steel tapered shaft (B) which was 8½" long and 1¼" in diameter at the head going to ¼" diameter at the lower end. The transducer was a Mullard 1" × 1¼" laminated " Permandur " magnetostrictor with a maximum power output of 2 kw. Although the mica interleaving reduces power losses due to eddy-current effects, it was necessary during operation to cool the head by forced convection with an air-blower. The energy to drive the magnetostrictor was obtained from an oscillator and a power amplifier to give 100 v output at a frequency of 20—30 kc./sec.; coupled to this was a D.C. polarizing current of 6 A at 10—25 v.

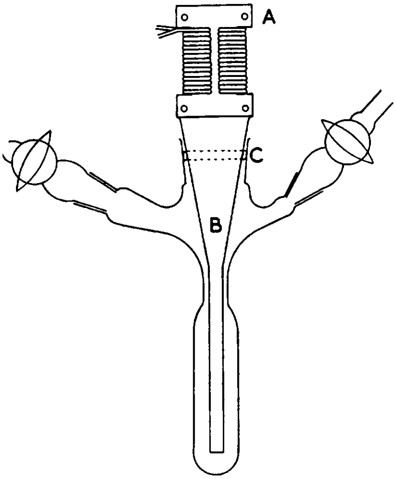

FIG. 1. Ultrasonic activator and reaction cell.

The alternating-current output was tuned to give maximum resonance with the magnetostrictor at 25 kc./sec. Although 1000 w could be supplied to the transducer, under normal operation only 400—600 w were necessary to bring about complete reaction. This high efficiency was helped by the tapered design of the probe and the narrow reaction cell. After 5—10 minutes' activation the whole solution attained the colour of the complex. During further activation of the benzacridines a number of different colour changes were observed which bore no obvious relation to the ultimate composition attained (as found by analysis).

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[6] Parkyns and Ubbelohde, *J.*, 1960, 4188.

[7] Down, Lewis, Moore, and Wilkinson, *Proc. Chem. Soc.*, 1959, 209.

It seems likely that these colour changes were due to self-complex-formation, between benzacridine which had not yet reacted and its mono- or di-negative ion. Prolonged ultrasonic activation (2 hr.) was necessary in order to afford the disodium derivatives of naphthacene and 1,2- and 3,4-benzacridine. However long the reaction, at the concentrations used only the monosodium derivative of 2,3-benzacridine and 1,2-benzanthracene could be prepared.

Solid complexes were obtained solvent-free by transferring the reaction vessel, after removal of the probe, to a high-vacuum line flushed with nitrogen. The whole was cooled in liquid nitrogen and the system evacuated to 10^{-4} mm. of mercury. The vacuum system contained two traps cooled by liquid nitrogen to collect the dioxan which evaporated from the complex as the temperature was slowly raised. When the powder was dry the temperature was raised to 180° to remove any strongly held dioxan. In preliminary experiments, where complex formation had not been taken to completion, some hydrocarbon sublimed from the powder at this temperature, but when formation of either the mono- or the di-sodium complex had been completed no sublimation could be observed. In a number of cases the temperature was raised to 500°; except for some darkening or charring near the limiting temperature no decomposition was observed.

Normally, after being kept at 180° for 1 hr. for removal of the last traces of dioxan, the complex was sealed into the lower half of the reaction cell at the constriction, until it was required for measurements.

Preparation of Complexes from the Vapour Phase.—To afford isoviolanthrene complexes with alkali metals use was made of the high m. p. and sublimation temperature, by treating the solid hydrocarbon with metal vapour.

The alkali metals were purified by distillation under a high vacuum, to remove hydrocarbon oils and gross impurities, and were sealed into ampoules containing about 0·5 g. of metal. Preparation of the complexes was carried out by a modification of the method of Fredenhagen and Suck,[8] adapted by McDonnell, Pink, and Ubbelohde.[9] The materials were contained in a tube similar to that previously described (cf. Fig. 2 of Part VI). Because alkali-metal vapours attack Pyrex glass, the reaction tube was made of soda glass with a protective layer flashed-on (NA 10 glass, G.E.C., Wembley). Whilst still open, the reaction tube was flushed with dry nitrogen, and the ampoule containing the alkali metal was cracked and placed in its open end. After this open end had been sealed, the alkali metal was distilled under a vacuum into the adjacent section of the tube. The pair of sections containing the alkali metal and the hydrocarbon, respectively, were then sealed off; reaction was brought about by placing the hydrocarbon and alkali metal ends of the sealed tube in two different furnaces. Different temperatures and reaction times were used for different preparations; in a typical preparation the hydrocarbon was heated at 450° and the potassium at 430° for 30 hr. Both ends of the tube were then allowed to remain at 400° for a further 12 hr. and the potassium tube was then sealed off. The distribution of alkali metal in the powder was allowed to reach uniformity during a further 24 hours' heating at 400°.

Unless otherwise stated, all operations involving transfer of the solid complexes were carried out in a nitrogen-filled dry box.

Construction of Dry Box.—This box was modified from a commercially available glove box (John Bass & Co.) of about 8 cubic ft. capacity. The principal change was to introduce a scavenging device, based on the ideas of Gibb,[10] for removing traces of oxygen or water that may enter during the operations at leaks or by diffusion through the rubber gloves. A continuous circuit of brass pipe, 2" in diameter, was constructed underneath the box with its inlet and outlet at opposite sides. Nitrogen was forced round this circuit and through the box by a concentric centrifugal fan (Airmax Ltd.). A gas-tight brass pot, about 8" in diameter, was inserted in the middle of the circuit beneath the box. One electrode, whose height could be adjusted, protruded through the detachable lid of the pot and another through its side. The side electrode was connected by a piece of copper wire to a porcelain dish containing solid sodium and placed inside the pot. An arc was struck by applying about 1000 v A.C. between the sodium in this dish and the top electrode; the current (about 1 A) was controlled by a choke of nominal 5 H inductance. By running this sodium arc continuously any access of oxygen or moisture to the box could be rapidly scavenged. At the beginning of an experiment, the dry

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[8] Fredenhagen and Suck, *Z. anorg. Chem.*, 1929, **178**, 353.
[9] McDonnell, Pink, and Ubbelohde, *J.*, 1951, 191.
[10] Gibb. *Analyt. Chem.*, 1957, **29**, 584.

box was filled with nitrogen by inflating a large metereological balloon (500 g. size) inside the box and then deflating it by admitting nitrogen to the box itself. The mouth of this balloon was accessible from the outside. This operation was repeated, after which the sodium arc was operated continuously to remove remaining traces of air or water. Initial conditioning of the box required 7—14 days. To minimise diffusion of oxygen from the outside, the inside of the box was kept at a positive pressure of pure nitrogen (30—40 mm.). When they were not in use, the glove holes were sealed by metal discs over rubber gaskets. The purity of the internal atmosphere was indicated by the length of time a freshly exposed piece of sodium remained bright. Under favourable conditions, manipulations could be completed in about 10 min.; perceptible tarnishing of freshly cut bright sodium might occur in about 1 hr.

Measurements of Density of Complexes.—These were made by means of a 10 ml. density bottle with liquid paraffin as densometric liquid. This paraffin was purified by bubbling pure nitrogen for a few hours through it at 120°. The complex (0·1—0·2 g.) was added to the density bottle, the stopper replaced, and the whole weighed. The complex was then quickly covered with paraffin and the bottle warmed to about 50° to remove entrapped nitrogen, then cooled to 20°, filled completely with paraffin, and reweighed. The density of the complex was calculated in the usual way.

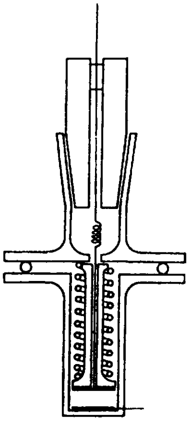

FIG. 2. Conductivity cell.

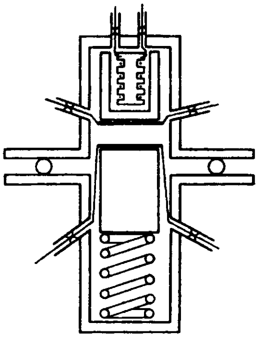

FIG. 3. Cell for measurement of thermoelectric power.

Measurement of Dark Resistance of Complexes.—A press was used for preparing pellets, 1—2 mm. thick, of the sample (cf. Parkyns and Ubbelohde [6]).

The special cell (Fig. 2) permitted subsequent measurements of resistance to be made outside the dry box. The central platinum lead was sealed with " Araldite " to prevent ingress of air, and was insulated by a hollow silica rod and silica stopper from the outside walls of the cell which were made of Pyrex glass. The use of silica enabled the resistance of compounds of the order of 10^{16} ohm cm. to be made if necessary (see preceding paper). The internal spring kept sufficient pressure (about 2 kg./cm.^{2}) on the platinum electrode to obviate surface contact effects arising from insufficient applied pressure on the pellet.

Most complexes gave satisfactory and cohesive pellets when a screw press was used.[6] It was impracticable to give them the annealing treatment described for isoviolanthrone and isoviolanthrene, but this was unnecessary largely because of the very much lower resistance of the complexes. Particularly with isoviolanthrene a few of the complexes rich in alkali metal never gave cohesive pellets. Possibly, like some metal powders, they require higher pressures than can be obtained from a hand press. Fortunately such complexes all gave pellets with very low electrical resistances ($\leqslant 100$ ohms); any dependence of activation energy on pressure appears to be within the experimental error of the present experiments.

After making and insertion of the pellet, the cell was assembled in the dry box and was tightened by means of circular clamps over a rubber O-ring. In this cell the pellets gave reproducible values of electrical resistance outside the dry box for at least 2 days.

Resistances were measured in the temperature range 30—100° in a copper air-thermostat as described previously.[6] The central lead of the cell was taken to the high-resistance terminal of the electrometer within a metal tube which provided electrostatic screening. The other lead went to the other terminal of the electrometer and was earthed. After change of temperature, about 30 min. was allowed before measurement at any altered temperature was made; results were reproducible to ±1%.

Effects of Decomposition of Complexes.—With these alkali-metal complexes, the resistance of which is much lower than that of the parent hydrocarbons, the slow relaxation effect observed previously [4] (cf. preceding paper) was very little in evidence. Generally, the lower the resistance of the complex the smaller the time required to reach a steady value. With isoviolanthrene complexes no relaxation at all was observed and the final value of resistance was attained at once.

In view of the very low resistances attained as a result of complex formation, it was desirable to verify that the conductivity observed was not due to ions arising from surface decomposition of the complex by water or oxygen. Accordingly, certain pellets were exposed to the air for a few seconds. In every case the electrical behaviour was completely altered. A very marked relaxation effect was then observed on application of the voltage, and the resistance did not reach a steady value for several minutes. Both the resistance and the activation energy of the exposed pellets were increased; when the applied measuring voltage was removed an e.m.f. appeared of opposite polarity to that originally applied. These are the characteristics to be expected from polarisation resulting from ionic conduction. Their absence in the undecomposed complex was taken as a criterion of purity and supports the view that the conductivity of the pure complexes is electronic before decomposition occurs.

Measurement of Thermoelectric Power (T.E.P.).—The cell illustrated in Fig. 3 was used for the measurement of T.E.P. of the alkali-metal complexes. A pelleted sample of the complex was placed in the cell and the two halves, separated by a neoprene O-ring, were clamped together in the same way as in the measurement of conductivity. This again enabled measurements to be made outside the glove box.

The walls of this cell were made of Pyrex glass, which provided sufficient insulation since the highest resistivity of complexes was 10^{11} ohm cm. at room temperature. The electrodes were made of 0·02″ platinum sheet, hard-soldered on to copper cylinders which acted as efficient heat sinks. One of the blocks was hollow and contained a resistance heater wound non-inductively on asbestos insulation. The other block rested on a metal spring to provide firm contacts with the pellet sample. Two leads (0·015″ in diam.) were fused to each platinum metal electrode, one of pure platinum and the other of 87 : 13 platinum–rhodium thermocouple wire. Suitable outside connections enabled the temperature of the electrodes to be measured, with the reference junctions cooled in ice–water. A steady temperature difference was maintained and the thermal e.m.f. across the pellet was measured directly on a Vibron electrometer. Voltages below 1 mv could not be measured accurately, so that fairly large temperature differences were required across the sample to give measurable thermal voltages. For the majority of sodium complexes the T.E.P. was so small that the deflection gave only the sign of the thermal electric current; this was always negative with respect to the cold junction, indicating in these solids that the predominant current carriers are negative.

Where the sample was exposed to the atmosphere for a short period (deliberately or accidentally), the T.E.P. apparently became large and positive with respect to the cold junction. A large standing e.m.f. was produced on the crystal and was obviously due to surface decomposition and polarization of the sample.

The results of conductivity, thermal electric power, and molar volume measurements of the metal aromatic complexes are given in Parts VI [5] and VII,[1] along with results of similar measurements on the pure hydrocarbons and their acceptor complexes.

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