63. *The Structure of Molecular Compounds. Part VII. Compounds formed by the Inert Gases.*

By H. M. Powell.

Preparation and some properties of the clathrate compound of argon and quinol are described. By crystallisation from water under 40 atmospheres' pressure of argon large and stable crystals containing nearly 9% by weight of argon are obtained. On heating they are converted into α-quinol with liberation of the argon. The volume of argon measured at room temperature and pressure is more than seventy times that of the crystals. Solution of the crystals liberates the gas. Other possible inert-gas compounds are discussed.

In the general series of molecular compounds of formula $3C_6H_4(OH)_2,M$, the component M may be argon. The first preparation of the *compound* was made by slow cooling of a solution of the components in benzene under 20 atm. pressure of argon (Powell and Guter, *Nature*, 1949, **164**, 240). The solvent was chosen as a result of previous experience in preparing the compound of quinol with carbon dioxide (Part IV, *J.*, 1948, 61), but the use of benzene results in a comparatively small yield owing to the low solubility of quinol in this solvent. The compound, being of the clathrate type, must be made from a solution containing dissolved molecules of the gas in sufficient concentration to cause the quinol molecules to separate out on cooling in the hydrogen-bonded cage form described as the β-quinol type of structure (Palin and Powell, Part VI, *J.*, 1948, 815). This form, different from the ordinary α-quinol, is produced in the presence of an appropriate concentration of a second component whose molecules are of suitable size to stabilise the cage structure in which they are enclosed.

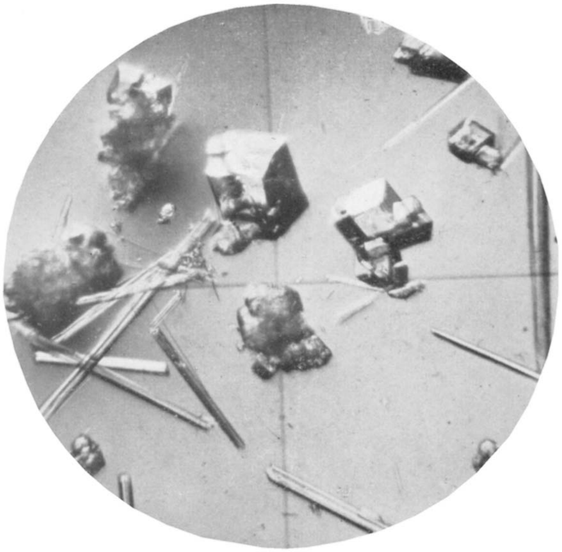
The present communication deals with new preparations and some properties of the products. The objects of these preparations were to obtain larger quantities of the material, to improve its purity, and to grow large single crystals for other investigations.

In order to obtain a greater concentration of quinol than is possible in a benzene solution, ethanol or water was used as solvent. Methanol was avoided since its molecules, in contrast with those of ethanol, are small enough to be enclosed to form the compound discussed in Part V (Palin and Powell, *J.*, 1948, 571). Water, which is used as solvent in the preparation of the quinol–sulphur dioxide compound, does not give a compound with quinol, but it was at first avoided since it had proved to be unsuitable in an attempted preparation of the carbon dioxide compound at a pressure of 50 atm. However, on trial with argon at somewhat lower pressure it has so far proved to be the best solvent.

The general method of preparation consists in making a solution of quinol saturated at room temperature, placing about 30 c.c. of this in a stainless-steel pressure vessel together with a further portion of quinol approximately equal in weight to the desired yield of compound, washing out atmospheric gases, and applying a pressure of argon from a cylinder, raising the temperature by heating the vessel in a large water-bath, and then allowing the solution to crystallise by slow cooling. The argon pressure is maintained by suitable additions from the cylinder.

The quantity of quinol taken should be such that it will dissolve when the temperature is raised. Usually much less was used than would have dissolved, and even so, considerable amounts of α-quinol sometimes came out with the compound. This is presumably due to a too rapid deposition of material with local impoverishment of the solution with respect to argon. The formation of the crystalline product takes place in the last stages of the cooling.

The need for a high pressure of argon is due to the low solubility of the gas. In the absence of any strong interaction between argon and quinol, the clathrate compound is formed by arranging for an argon atom to be available in position at the surface of the growing crystal whenever a cage of quinol molecules links up through its hydrogen bonds. The pressure is not required to prevent dissociation, since once the argon atom is enclosed it is retained by the strength of its cages, so that if sufficient time were allowed for the growth of the crystal it might form from a solution of very low argon concentration. For ordinary rates of crystallisation, obtained by allowing the water-bath to cool in the air, the pressure required to prevent local impoverishment of the solution might be expected to be of the same order of magnitude as that which the argon contained in the crystalline product would have if its cage surroundings were removed. From the known dimensions of the cages, which vary slightly but in a predictable way according to the dimensions of the enclosed molecule (Part VI), the volume of crystalline substance of formula $3C_6H_4(OH)_2,A$ which contains one g.-atom of argon is calculated to be approximately 260 c.c. This quantity of argon in the form of a gas



Photomicrograph of part of a mixed product. The large rhombohedra are crystals of the argon–quinol compound. The needles are α*-quinol. Magnification* × **40.**

[*To face p.* 299.

occupying the same volume at 15° has a calculated pressure of 91 atmospheres. The present series of preparations has been made with argon at pressures up to 40 atmospheres. As is commonly the case with compounds of this type (Part VI), the quantity of argon is below that corresponding to the ideal formula owing to some cavities being left empty. The product of highest argon content so far obtained has the composition $3C_6H_4(OH)_2,0{\cdot}8A$, and therefore contains argon equivalent to a pressure of 73 atmospheres.

Observations on some prepared samples are given below. Argon contents were determined either from the weight of quinol recovered after liberation of argon by dissolution of the material in ether, or by heating the substance to 130°. For heating, the material is contained in a closed vessel to avoid loss of quinol which slowly sublimes. After the vessel has cooled, the liberated argon is displaced by air, and the weight of quinol residue determined. The nature of the crystalline samples was also examined in other ways. Crystals of the quinol–argon compound liberate large volumes of gas when covered with methanol which dissolves quinol, and, although α-quinol crystals sometimes give off a small amount of gas, there is no difficulty in distinguishing the two. With the aid of the microscope, or without it in the case of large crystals, the argon–quinol crystals may be recognised by their stumpy hexagonal prism form with terminal rhombohedral faces, or by their occurrence as rhombohedra of the type illustrated in the photomicrograph. Crystals of α-quinol were always very thin hexagonal needles, often striated lengthwise, and their terminal faces were usually indistinct. Differences in refractive indices could be used to distinguish the two materials but were not much employed since they are affected by the variation in composition of the compound. Single-crystal *X*-ray photographs give a sure proof of the presence of a component, and powder photographs were also employed for identification since a more representative sample of a mixed product is obtained by powdering a larger quantity. A preliminary trial showed that the compound is not affected by powdering. Differences of density make it possible to separate the constituents by flotation, but this procedure is not very effective since the densities vary on account of variable composition, occlusions in the crystals, and the tendency of the crystals to form aggregates.

EXPERIMENTAL.

(1) From 60 c.c. of benzene solution at 34 atm., 0·4 g. of product [Found : A, 4. Calc. for $3C_6H_4(OH)_2,A$: A, 10·8%] was obtained. The product contained needle-shaped α-quinol together with larger crystals of the argon compound in the form of rhombohedra. The difference is shown in the photomicrograph. As far as possible a mechanical separation was made. Both types of crystal are colourless and some of the argon-containing crystals are more needle-like than those shown in the photograph. This makes the separation difficult and the analysed portion is of uncertain purity.

(2) From 30 c.c. of ethanol solution at 40 atm., 5 g. of product (Found : A, 3·5%) were obtained. The crystals were of needle habit but usually of a more stumpy appearance than those of α-quinol, from which they may also be distinguished by their terminal rhombohedron faces when these are visible. The product contained some α-quinol.

A glass apparatus was constructed so that a known weight of the product could be placed in a bulb. A space above the crystals could be evacuated by means of a Hyvac pump and then isolated from the pump by a tap. The space, consisting of bulb and connecting tubes, was bounded by the surface of mercury in an attached manometer, and could be restored to a fixed volume by manipulation of the manometer until this mercury surface reached the fixed mark attained when the system was first evacuated. The volume of this space was determined by observing the temperature and pressure when a known mass of air was admitted from a second bulb, and, after the apparatus had been dismantled, was checked by the weight of water required to fill it, with allowance for the volume of crystals.

When the bulb containing a portion of the compound was heated slowly, the evolution of argon could be followed by observation of the manometer. The pressures observed were not equilibrium pressures and at any time the mercury level could be restored to its original position in order that the pressure might be read for a fixed volume of gas. After the evolution of gas at higher temperature, lowering of the temperature to a former value did not result in a decrease in pressure to the value previously observed at the lower temperature. At 40° gas was given off very slowly, the pressure being 1 mm. (compared with 762 mm. when all argon was liberated). At 70° a pressure of 29 mm. was observed, and this rose in the course of 5 minutes to 39 mm. Forty minutes later, after the temperature had been taken to 100°, the pressure recorded on restoring the temperature to 70° was 391 mm. The liberation of argon is very nearly complete at 130°, and at this temperature the solid has been converted into α-quinol. Raising the temperature until the quinol melts causes no appreciable change in the total amount of gas. The final pressure of the gas, at the fixed volume, was measured at room temperature, and, since the mass of gas liberated from the original weighed quantity of material was known, the density of the gas was calculated. The values observed, 0·0019 g./c.c., were usually slightly higher than the density of argon (0·0018 g./c.c. at N.T.P.). The argon used was spectroscopically pure, and the discrepancy is probably due to the argon content of the specimen being slightly over-estimated. The behaviour has not been fully investigated but it is known that a slight loss of wieght occurs slowly when certain samples of the argon compound are kept either in the atmosphere or in a desiccator. It may be due to the removal of small amounts of adhering solvent or to the escape of some argon. In either case this would mean that the true argon content of a sample from which the argon was released and measured would be less than that derived from an analysis carried out before the material was used, and thus would lead to a high value for the density.

(3) From 30 c.c. of aqueous solution at 40 atm., the argon–quinol compound was obtained in large single crystals in the form of hexagonal prisms with terminal rhombohedron faces. Some of these crystals were nearly 1 cm. long and several mm. in breadth. They were accompanied by crystals of α-quinol which always form as very thin needles. Separation of the two products could therefore be carried out by hand picking or by sieving, and the two parts examined separately. With other conditions kept as far as possible the same, the weight of product was varied by variation of the quantity of quinol used in the preparation. A yield of 6 g. was separated into nearly equal weights of α-quinol and the compound; one 3-g. yield contained at least 2·9 g. of the compound and very little α-quinol. However, the relative amounts of α-quinol and the compound obtained in different preparations in similar conditions were not constant, and it seems probable that the proportions are sensitive to conditions such as the frequency of formation of crystal nuclei which were not accurately controlled. However, the great ease of separation of the two constituents as formed from aqueous solution ensures an uncontaminated yield of the compound. The argon content in a typical sample was 8·8%, corresponding to 80% of the maximum possible argon content. An even greater proportion of occupied cavities may be expected with the more soluble heavier inert gases and the corresponding xenon compound should contain as much as 28% by weight of the inert gas.

Crystals of the argon compound have been preserved for weeks without visible change but some samples have been observed to lose weight, so far less than 1%. Some time will be necessary for the further examination of the keeping properties of the compound. Small quantities of solvent, which by successive attacks on different parts of the structure may detach quinol molecules, may cause the liberation of argon. It seems probable that in suitable conditions the compound would be a convenient portable source of argon, and the compounds of the heavier inert gases could be used similarly. The fact that the stable compound already prepared retains argon effectively at more than 70 atm. pressure is sufficient demonstration of the reality of the imprisoning action which is the basis of the concept of clathrate compounds. A fuller description of the relation of the argon atom to its surroundings is to be given with the crystal structure determination of the compound.

Some preliminary experiments were made concerning other possible compounds of similar type. All were carried out with 40 atm. pressure of inert gas, and in every case a preparation which had resulted in the formation of the argon compound was repeated with the substitution of another substance for quinol or for argon. The crystalline products were dissolved in suitable solvents and in no case was there any evolution of inert gas. Thus no compound was formed between argon and resorcinol, *p*-aminophenol, or *p*-phenylenediamine from ethanol solutions. Substitutes for quinol may be found among other substances capable of hydrogen-bond formation or in other classes of compound, but any exact prediction does not seem possible at present. No compound was formed between quinol and helium from benzene solution. The product was identified as α-quinol. This expected result may be explained by the small effective size of the helium atom, well known for its power of penetrating small spaces. The compound does not form because the helium atom cannot be retained by the quinol cages. A further attempt to prepare the helium–quinol compound in more favourable conditions is projected. It is not known whether neon will give a compound with quinol; it seems certain that the heavier inert gases will do so. Examination of these possibilities is intended.

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UNIVERSITY MUSEUM, OXFORD.

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