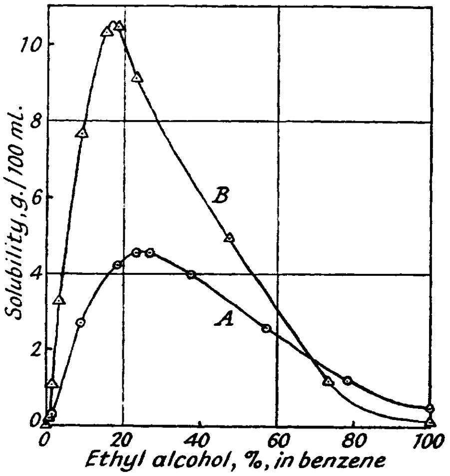
450. *Complexes of Copper Phenylacetate and Diphenylacetate with Alcohols.*

By Malcolm Crawford.

Copper phenylacetate and diphenylacetate are insoluble in benzene but dissolve readily when small amounts of other organic compounds, particularly alcohols, are added. This is attributed to the formation of complexes, many of which have in fact been isolated in the solid state and studied. Suggestions are made with regard to their constitution.

Copper salts of many carboxylic acids are sufficiently soluble in benzene to impart to it a pale green colour. Only rarely is the solubility great enough to give a deep green solution. Copper phenylacetate, for example, is practically insoluble in benzene, but is slightly soluble in absolute ethyl alcohol (0·5 g. in 100 ml. at 25°). In the mixed solvents, however, the solubility is considerably greater, reaching a maximum of 4·5 g. in 100 ml. of 25% alcohol in benzene at 25°. The solubility curve is shown in Fig. 1.

Fig. 1.



A, *Copper phenylacetate.*
B, *Copper diphenylacetate.*

This behaviour indicates the likelihood of compound formation, yet when the solution in the mixed solvents is concentrated, the green needle crystals which separate on cooling consist of copper phenylacetate alone. The same effect is observed with other alcohols, such as *n*-propyl, *n*-butyl, and allyl, but in none of these cases have compounds been isolated.

Solubility data for copper diphenylacetate are also included in Fig. 1. In this case the effect is still more enhanced. The solubility in the pure solvents is negligible, but in 17% alcohol in benzene it reaches a maximum of 10·6 g. in 100 ml. at 25°. In addition to this, crystallisation from alcohol-rich mixtures gives light-green octahedral crystals containing two molecules of combined alcohol. From alcohol-poor mixtures dark-green needle crystals of copper diphenylacetate separate.

If the octahedral crystals are filtered off and stored in slightly damp condition they can be kept indefinitely, but on drying and exposure to the atmosphere they gradually lose alcohol over a period of a few weeks. When all the alcohol is gone the octahedral form remains intact but the colour has changed to a darker green. The solubility in benzene has also vanished. There would seem, therefore, to be little doubt that the enhanced solubility in the mixed solvents is due to compound formation.

Most other alcohols tested behave similarly to ethyl alcohol Table I lists the compounds examined and the alcohols tested; some of these compounds were mentioned in a preliminary note (*Nature*, 1947, **160**, 19). It will be seen that several primary alcohols, *viz.*, *n*-propyl, allyl *n*-butyl, and *iso*butyl, form light-green octahedral crystalline compounds containing two molecules of alcohol similar to that formed by ethyl alcohol. All of them lose the combined alcohol within an hour at 100°, but at room temperature the allyl alcohol compound loses weight more slowly than the others in spite of the similarity in volatility of allyl and the other alcohols. This compound is therefore more stable.

TABLE I.

Compounds of copper diphenylacetate with various alcohols.

	Compound.			
Alcohol.	Crystalline form.	Colour.*	Stability.	Mols. of combined alcohol.
Methyl	Plates	Dark	Medium	1½—2 (variable)
Ethyl	Octahedra	Light	,,	2
n-Propyl	,,	,,	,,	2
Allyl	,,	,,	More stable	2
n-Butyl	,,	,,	Medium	2
*iso*Butyl	,,	,,	,,	2
n-Amyl	,,	,,	,,	1½
n-Hexyl	—	—	(No compound)	—
Benzyl	Needles	—	Very stable	2
n-Octadecyl	—	—	(No compound)	—
*iso*Propyl	—	—	,,	—
sec.-Butyl	Prisms	Dark	Very stable	Indefinite
*cyclo*Hexanol	Needles	—	,,	1
tert.-Butyl	Rhombs	Dark	,,	2
tert.-Amyl	Needles	—	,,	1
Triphenylcarbinol	—	—	(No compound)	—

* Colour only recorded where markedly light or dark green.

In the preparation of the *n*-amyl compound appropriate seeding of the supersaturated solution will produce either solvent-free needles or octahedra containing only 1½ molecules of the alcohol.

Neither of the larger primary alcohols tested, *n*-hexyl and *n*-octadecyl, was found to combine with copper diphenylacetate.

Benzyl alcohol forms a compound crystallising in needles. Its high stability may be due, at least in part, to the very low volatility of benzyl alcohol. The methyl alcohol compound is also exceptional in the crystal form, plates, and in its variable composition.

Among secondary alcohols, *iso*propyl alcohol could not be induced to form a compound, whereas *sec.*-butyl alcohol gives a dark green compound of indefinite composition, containing about 0·6 mol. of the alcohol, and of such stability that the alcohol could not be driven off entirely even after many hours' heating at 100°. *cyclo*Hexanol forms a 1 : 1 compound in needles, so stable that it required 7 hours at 100° to remove all the combined alcohol.

The two compounds with tertiary alcohols which have been examined are of high stability. That with *tert.*-butyl alcohol contains two molecules of the alcohol (rhombs), and that with *tert.*-amyl alcohol contains only one molecule of alcohol (needles). Neither loses weight on standing in air. No compound could be obtained from triphenylcarbinol.

The solubility in benzene and other hydrocarbon solvents ought to allow of easy determination of the molecular weight of these compounds. Difficulties arise, however, owing to the very low solubility in pure benzene. From the curves in Fig. 1 it can be seen that 1% or 2% of an alcohol must be present in the solvent before the solute reaches a concentration sufficient to give a satisfactory depression of the freezing point. The combined alcohol is insufficient to accomplish this. Nevertheless it is possible to prepare supersaturated solutions by dissolving the crystals in hot benzene, then cooling the solution and determining the depression before solute crystals separate.

TABLE II.

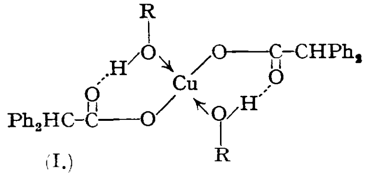
Molecular weight of copper diphenylacetate–diethanol complex in benzene at the freezing point.

Concn. of substance, % (w/w)	0·57	1·21	2·06
Δ	0·080°	0·159°	0·247°
M	358	386	426

Calc. for $C_{28}H_{22}O_4Cu,2C_2H_6O$: M, 578.

It will be seen from Table II that the ethyl alcohol compound is dissociated in benzene at its freezing point. It is probable but not certain that the compound contains one atom of copper in the molecule both in solution and in the solid state. The structure (I; R = Et) is suggested as probable.

The study of this series of complexes may help to throw light on certain aspects of solubility, particularly solvation and solubility in mixed solvents. The insolubility of copper diphenylacetate in benzene is not surprising. It is probably not so much due to the fact that it is a salt as that it is associated in the solid state to large stable molecules, either by ionic forces or by co-ordinate linkages, but certainly not by van der Waals forces alone.


(I.)

In the presence of alcohol, however, disaggregation to small molecules takes place because the monomeric molecule combines with the alcohol in preference to associating with itself. The resulting small molecules of the type (I) are soluble in benzene, as might be expected since the hydrophilic groups are screened by a hydrocarbon exterior and dissolve, therefore, like any hydrocarbon.

Work in progress (*Nature*, 1950, **165**, 728) shows that isolable complexes with alcohols are formed by the copper salts of several other organic acids. No complexes of copper phenylacetate can be isolated although from Fig. 1 they obviously exist in solution. It is likely that the particular stability of the copper diphenylacetate complexes is due to the shape of the molecule, which permits small molecules to attach themselves by weak linkages and fit into holes in the crystal lattice. This would be impossible where R in the alcohol ROH is too long or too bulky. The limit of length in this case would appear to be *n*-amyl alcohol, which is just too large to fill all the spaces available This does not necessarily apply in solution. Large alcohol molecules would still facilitate solution of copper diphenylacetate in benzene, but no stable crystals would be isolable, as indeed is found with *n*-hexyl and *n*-octadecyl alcohols. The very bulky alcohol, triphenylcarbinol, however, does not enhance the solubility of copper diphenylacetate in benzene, presumably because for steric reasons it cannot form a complex even in solution.

We have here cases of solvation where the actual number of solvating molecules can be assessed together with indications of the forces likely to be involved in the process, namely, hydrogen bonding and co-ordinate linkage aided by steric conditions allowing approach and assisting retention of the attached molecules even into the solid state.

Compounds of copper diphenylacetate with various ketones, aldehydes, esters, and amines have also been isolated, and will be described later.

EXPERIMENTAL.

Materials.—Copper diphenylacetate was prepared by mixing equivalent amounts of A.R. copper sulphate and sodium diphenylacetate, both in aqueous solution. The bulky green precipitate was well washed, dried at 100°, and crystallised from benzene–ethyl alcohol (4 : 1). After being washed, the needle crystals were dried at 100° (Found: Cu, 13·0, 13·0. Calc. for $C_{28}H_{22}O_4Cu$: Cu, 13·09%). Copper phenylacetate was prepared in similar fashion (Found : Cu, 19·0, 19·1. Calc. for $C_{16}H_{14}O_4Cu$: Cu, 19·05%).

The various liquid alcohols used were fractionally distilled, and a middle fraction selected. Triphenylcarbinol and *n*-octadecyl alcohol were purified by recrystallisation. The compounds for examination were obtained by heating copper diphenylacetate with the alcohol in question, benzene being added if necessary to effect solution. On cooling the solution the compound separated. In difficult cases most of the benzene had to be distilled off before cooling. The compounds were filtered off, washed with the alcohol and stoppered in tubes without drying. Occasionally alcohol-free copper diphenylacetate separated. The preparation was thereupon repeated more alcohol being used.

Methods.—The amount of combined alcohol was determined by loss of weight on heating at 100°. The initial dry weight of each sample was obtained by a process of " continuous weighing " (see Guichard, *Bull. Soc. chim.*, 1944, **11**, 63). A quantity of the substance is placed on a weighed watch glass and weighed at regular intervals. The weight is plotted against time. In the curve (Fig. 2) the rapid loss of adhering alcohol is represented by an initial steep fall, then there is a sharp break followed by gradual loss of combined alcohol. The point at which the two parts of the curve intersect gives fairly accurately the original dry weight of the compound. From the second part of the curve the rate of loss of combined alcohol can be used to gauge the stability.

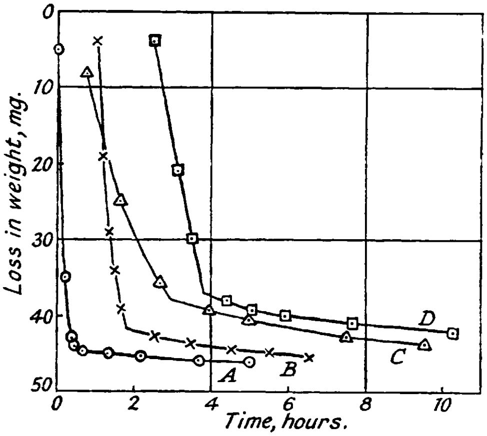
All copper determinations were performed gravimetrically by means of salicylaldoxime. Volumetric methods were unreliable and required larger amounts of the substance.

The solubility determinations were made by shaking excess of the substance with solvent in a closed vessel in a thermostat at 25° for one or two days or until two samples removed by pipette with filtering at one-day intervals agreed in dry weight after evaporation of the solvent. This method is sufficiently accurate for the purpose.

Copper Phenylacetate.—The determinations of solubility in alcohol–benzene mixtures are recorded in Fig. 1.

Complexes.—Copper phenylacetate was dissolved by warming separately with the following alcohols with the addition of benzene where necessary: *n*-propyl, *n*-butyl, *tert.*-butyl, allyl. On cooling, the crystals which separated were filtered off, washed with the appropriate alcohol, and subjected to continuous weighing to give the initial dry weight and then heated at 100°. The loss in weight on heating was: *n*-propyl alcohol, 0·63; *n*-butyl alcohol, 0·19; *tert.*-butyl alcohol, 1·58; allyl alcohol, 3·76%. The losses are very small and show that there is no combined alcohol in the crystals, but that the allyl alcohol is more adherent than the others. There is no compound with ethyl alcohol, as the copper phenylacetate was obtained from that solvent as already described.

FIG. 2.



A, *Ethyl alcohol.* B, n-*Propyl alcohol.* C, n-*Amyl alcohol.* D, n-*Butyl alcohol.*

Copper Diphenylacetate.—The solubility determinations are recorded in Fig. 1.

Complexes.—Analytical data relating to the *complexes* isolated are given in Table III.

TABLE III.

Complexes of copper diphenylacetate with alcohols.

	Loss in wt. on heating, %.		Copper, %.		Copper, %, after heating.	
Complex.	Found.	Reqd.	Found.	Reqd.	Found.	Reqd.
Diethanol	15·6, 16·1 15·9, 15·9	15·93	11·0, 10·8	11·0	13·0, 12·9	13·09
Di-*n*-propanol	20·5	19·83	—	—	—	—
Diprop-2-enol	19·5	19·30	—	—	—	—
Di-*n*-butanol	21·8, 21·7 20·5, 21·3	23·37	10·2, 10·4	10·03	12·9, 13·2	13·09
Di-2-methylpropanol	22·2, 23·9	23·37	—	—	—	—
Di-2-methyl-2-propanol	23·0	23·37	—	—	—	—
Sesqui-*n*-pentanol	21·3, 21·0	21·38	10·4, 10·4	10·29	13·2, 13·1	13·09
2-Methyl-2-butanol	15·3, 15·1	15·35	—	—	—	—
Di*cyclo*hexanol	17·1	17·25	—	—	—	—
Bisphenylcarbinol	29·2	30·8	—	—	—	—
Methanol (sesqui-di):						
Preparation A	8·79, 8·75 0·86 *	9·00 (1½)	1·8	11·91 (1½)	13·0	13·09
Preparation B	10·23, 10·24	11·65 (2)	11·7, 11·7	11·65 (2)	13·1, 13·1	13·09
2-Butanol			12·0	11·4		

* After standing for 8 months in contact with methanol.

The following alcohols failed to yield compounds.

iso*Propyl alcohol.* On concentration of a solution of copper diphenylacetate in benzene–*iso*propyl alcohol, fine dark crystals separated (Found: Cu, 12·8; loss on heating, 1·67; Cu, after heating, 13·1. Calc. for $C_{28}H_{22}O_4Cu$: Cu, 13·09%). The crystals were therefore copper diphenylacetate with a small amount of adhering solvent.

n-*Hexyl alcohol.* A solution of copper diphenylacetate in a mixture of *n*-hexyl alcohol and benzene was distilled until most of the benzene had been removed. On standing for several days, green crystals of copper diphenylacetate separated (Found: Cu, 13·0, 13·0; loss on heating, 0·4, 0·4; Cu, after heating, 13·1, 13·1. Calc. for $C_{28}H_{22}O_4Cu$: Cu, 13·09%).

n-*Octadecyl alcohol.* Copper diphenylacetate dissolved in a heated solution of *n*-octadecyl alcohol in benzene. On cooling, the alcohol crystallised out together with a small amount of dark green needles having the characteristic appearance of copper diphenylacetate.

Triphenylcarbinol. A solution of triphenylcarbinol in benzene dissolved copper diphenylacetate only to the slightest extent.

WIGAN AND DISTRICT MINING AND TECHNICAL COLLEGE.

[*Received, April 1st,* 1950.]