403. *The Relative Stability of Copper Derivatives of β-Diketo-compounds.*

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On addition of a β-diketone or a β-keto-ester to a benzene or chloroform solution of the copper derivative of another compound of either of these types, immediate colour changes are observed in many cases, such as would result from an equilibrium

$$CuA_2 + 2HB \rightleftharpoons CuB_2 + 2HA \quad . \quad . \quad . \quad (1)$$

where CuA_2 and CuB_2 have different colours. When the original copper compound is derived from either acetylacetone or dibenzoylmethane, no other copper compounds can be isolated from the solution, whatever diketo-compound is added; and conversely, the addition of either of these two diketones to a solution of the copper compound of any other diketo-compound produces an immediate precipitation of the corresponding copper derivative. In several other cases, either of the salts CuA_2 and CuB_2 can be obtained according to the conditions. Thus, addition of salicylaldehyde to a benzene solution of copper acetoacetic ester changes the colour from green to yellowish-green, but the original copper compound is recovered unless a considerable amount of salicylaldehyde is added, whereupon copper salicylaldehyde crystallises. Examination of a large number of cases showed that ordinarily the two copper compounds are the only solid products recoverable.

Since such equilibria give a means of measuring the relative stability of the chelate rings formed by diketo-compounds, we have investigated several cases quantitatively. Our results show that the reaction occurs in two stages,

$$CuA_2 + HB \rightleftharpoons CuAB + HA \quad . \quad . \quad . \quad (2a)$$
$$CuAB + HB \rightleftharpoons CuB_2 + HA \quad . \quad . \quad . \quad (2b)$$

and that, further, the copper compounds react together

$$CuA_2 + CuB_2 \rightleftharpoons 2CuAB \quad . \quad . \quad . \quad . \quad (3)$$

In two cases (HA = benzoylacetone; HB = ethyl acetoacetate or ethyl acetonedicarboxylate), we find that the compounds CuAB can exist as solids in equilibrium with solutions containing excess of CuA_2.

The colour changes and precipitations show that the reactions with the diketo-compounds are very rapid, an interesting result in view of the fact that they involve the rupture and formation of six-membered rings in the presence of an inactive solvent.

The only method available for investigating these equilibria is the estimation of the concentration of copper in solutions saturated with regard to one salt (CuA_2), using in different experiments the pure solvent, the solvent containing known amounts of the other diketo-compound (HB), and the solvent containing known amounts of the other copper compound (CuB_2). The solvent was benzene and the temperature 25°. At first, in spite of careful purification and drying of all the materials, no concordant results for the solubilities of the copper compounds could be obtained, and with the compounds from keto-esters obvious decomposition sometimes occurred during 48 hours' shaking. It was only when all distillations and transfers of material were carried out in dry air that consistent values were obtained. Excellent agreement was reached with the copper compounds of β-diketones, *e.g.*, six experiments, using two different preparations of copper benzoylacetone, gave values for the solubility of 0·0531—0·0534 mol./litre. With the copper compounds of β-keto-esters the agreement was less good, the worst case being acetoacetic ester, where three different samples of the copper compound gave values 0·0283, 0·0278, and 0·0280, each number being the mean of at least two closely agreeing results. An inspection of the numbers on p. 2707 will show that, throughout the work, the derivatives of the keto-esters gave less regular results than those of the diketones.

Although preliminary experiments were tried with many other copper compounds, only those derived from acetylacetone, benzoylacetone, dibenzoylmethane, acetonedicarboxylic ester, and acetoacetic ester were used, since these alone proved sufficiently stable.

That equation (1) is inapplicable is shown as follows. If S_{I} is the solubility of the salt CuA_2, and T is the concentration of copper reached by saturating a solution containing b of the diketone HB with CuA_2,*

$$T = S_{\mathrm{I}} + [CuB_2],\ [HA] = 2[CuB_2],\ \text{and } b = [HA] + [HB],$$

from which it follows that the equilibrium constant corresponding to equation (1) is given as

$$K' = 4(T - S_{\mathrm{I}})^3/\{S_{\mathrm{I}}[b - 2(T - S_{\mathrm{I}})]^2\} \quad . \quad . \quad (4)$$

The values of K' thus obtained showed continuous variation as b was altered, and in several cases the value of T was greater than equation (1) alone allows. Equation (1) being assumed, such a result could follow if (*a*) the solubility of CuA_2 is increased by the presence of other substances, apart from any chemical reaction, or (*b*) the copper compounds are associated in benzene solution, the degree of association necessarily increasing with concentration, or (*c*) addition compounds such as CuA_2,HB and CuB_2,HA are formed, or (*d*) the salts CuA_2 and CuB_2 form a compound CuA_2,CuB_2 in solution. But, as will be shown, equations (2a), (2b), and (3) explain the results without any of these assumptions.

Additions of various oxygen-containing substances in amounts comparable with the additions of the diketo-compounds, produce effects on the solubilities far too small to account for the discrepancies,

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* All concentrations of diketo-compounds and their copper compounds are expressed in mols./litre, and concentrations of copper are in g.-atoms/litre.

so that (*a*) is excluded; *e.g.*, copper acetylacetone, $S_{\mathrm{I}} = 0{\cdot}00338$, T for $0{\cdot}0327M$-ethyl malonate 0·00341, for $0{\cdot}0472M$-salol 0·00340; copper benzoylacetone, $S_{\mathrm{I}} = 0{\cdot}0533$, T for $0{\cdot}0675M$-ethyl malonate 0·0535. As regards (*b*), Urbain and Debierne (*Compt. rend.*, 1899, **129**, 302) found normal molecular weights in benzene for the acetylacetone compounds of aluminium, iron, cobalt, and manganese. We find similar results for the copper compounds of benzoylacetone, acetonedicarboxylic ester, and acetoacetic ester, the other two compounds being too sparingly soluble for examination. As regards (*c*) we have shown (see data below) that addition of either of the diketones HA or HB to a system containing both CuA_2 and CuB_2 as solid phases causes no change in concentration, such as must occur if (*c*) were the cause of the discrepancy.

That intermediate or double *compounds* such as CuAB or CuA_2,CuB_2 are formed, is proved by the fact that the copper concentration in a solution saturated with regard to both CuA_2 and CuB_2 (denoted later as S_{M}) is considerably greater in all cases than the sum of the separate solubilities. Thus, for copper acetylacetone with copper benzoylacetone the values found for S_{M} were 0·0878 and 0·0880; for S_{M} in presence of acetylacetone, 0·878 (two identical values), and the same value in presence of benzoylacetone. The sum of the separate solubilities is 0·0567. Further, the results which, by the methods described below, give values 5·4 and 5·3 for the equilibrium constant corresponding to equation (3), when HA = acetylacetone and HB = benzoylacetone, give 87 and 144 for the " constant " corresponding to the reaction $CuA_2 + CuB_2 = CuA_2,CuB_2$. With the same diketones for equation (1), which must apply if CuA_2, CuB_2, and CuA_2,CuB_2 are the only copper compounds present, the equilibrium " constant " K' falls continuously from 25 to 2·4, while values of the constant for equation (2a) from the same numbers are all between 1·9 and 2·1. Other cases give similar results. It appears certain, therefore, that there is no evidence in favour of any of the effects (*a*), (*b*), (*c*), and (*d*), and that equations (2a), (2b), and (3) apply, the corresponding mass-action equations being

$$K_1 = [\mathrm{CuAB}][\mathrm{HA}]/[\mathrm{CuA_2}][\mathrm{HB}] \quad . \quad . \quad (5a)$$

$$K_2 = [\mathrm{CuB_2}][\mathrm{HA}]/[\mathrm{CuAB}][\mathrm{HB}] \quad . \quad . \quad (5b)$$

and

$$K_1/K_2 = [\mathrm{CuAB}]^2/[\mathrm{CuA_2}][\mathrm{CuB_2}] \quad . \quad . \quad (6)$$

Equilibria involving only Copper Derivatives.—Values of K_1/K_2 can be calculated directly from S_{M}, for

$$S_{\mathrm{M}} = S_{\mathrm{I}} + S_{\mathrm{II}} + [\mathrm{CuAB}] = (\text{from } 6)\ S_{\mathrm{I}} + S_{\mathrm{II}} + \sqrt{S_{\mathrm{I}}S_{\mathrm{II}}K_1/K_2} \quad (7)$$

where S_{I} and S_{II} are the solubilities of CuA_2 and CuB_2 respectively, the solution being saturated with regard to both CuA_2 and CuB_2. They can also be calculated (second method) from the concentration of copper (T) reached at equilibrium by shaking a solution of a known amount (y) of one compound (CuB_2) insufficient for saturation, with excess of the other (CuA_2). For then

$$T = S_{\text{I}} + [CuAB] + [CuB_2] \quad . \quad . \quad . \quad . \quad (8)$$

and

$$y = [CuB_2] + [CuAB]/2 \quad . \quad . \quad . \quad . \quad (9)$$

so that both [CuAB] and [CuB_2] can be found and used in equation (6). Another independent series of results can be obtained, using the second method, by interchanging the functions of CuA_2 and CuB_2. In practice, the accuracy reached in the determination of S_{M} is greater than in the experiments with known additions of one copper compound, but the second method is useful for checking the first. Further, when either CuA_2 or CuB_2 is very sparingly soluble, small experimental errors cause large changes in the value of K_1/K_2 calculated by the second method. In such cases, verification of the value of K_1/K_2 from S_{M} can be made by using it to calculate the concentration of copper which should be reached in the experiments with known amounts of one copper derivative. For, from equations (6) and (9),

$$[CuAB] = \sqrt{yS_{\text{I}}K_1/K_2 + (S_{\text{I}}K_1/4K_2)^2} - S_{\text{I}}K_1/4K_2$$

so that [CuAB], then [CuB_2] from equation (9), and finally T, can be found. As an example, the numbers for copper acetylacetone (CuA_2) and copper acetonedicarboxylic ester (CuB_2) are quoted :

(*a*) K_1/K_2 from S_{M}, 4·62.

(*b*) Solutions saturated with regard to CuA_2 :

y (of CuB_2).	T (found).	K_1/K_2.	T (calc. from $K_1/K_2 = 4·6$).
0·0218	0·0324	4·2	0·0326
0·0328	0·0456	4·5	0·0457
0·0344	0·0476	4·6	0·0472
0·0404	0·0538	3·9	0·0545

Solutions saturated with regard to CuB_2 :

y (of CuA_2).			
0·00745	0·0619	1·8	0·0626
0·00938	0·0636	0·7	0·0660
0·01250	0·0692	2·4	0·0714

The agreement is as good as could be expected and confirms our equations.

For three pairs of compounds, *viz.*, copper benzoylacetone with copper acetylacetone and with copper dibenzoylmethane, and copper acetylacetone with copper acetonedicarboxylic ester, the value of S_{M} was independent of the amounts of CuA_2 and CuB_2 used, so long as they were in excess. In two other cases, *viz.*, copper benzoylacetone (CuA_2) with copper acetoacetic ester and copper acetonedicarboxylic ester (CuB_2), two distinct values of S_{M} were obtained. Thus, in the latter case S_{M} was found to be 0·239, 0·240, and 0·238 (HA present) in separate experiments with CuA_2 in excess, while with CuB_2 in excess the values were 0·228, 0·227, and 0·229 (HB present). In the former case the difference between the two values of S_M (0·139 and 0·132) is much less, but it is not possible to attribute this to experimental error since the value of K_1/K_2 deduced on the assumption of one invariant point disagrees with that found from known additions of one copper compound to the other, and further, the assumption of two invariant points has been otherwise verified (see p. 2701). It is necessary, therefore, to assume in these cases that a third solid, presumably CuAB, can exist in contact with solution, so that two invariant points are possible with CuA_2 + CuAB and CuB_2 + CuAB as the solid pairs.

Calculation of K_1/K_2 from the two values of S_M is possible but is even more affected by small experimental errors than calculation from known additions of one compound, which, therefore, has been used in these cases.

Equilibria involving Free β-Keto-compounds.—To get the values of K_1 and K_2, when K_1/K_2 is known, it is necessary to find T in a solution to which a known amount, b, of one of the diketo-compounds (HB) has been added and which has then been saturated with CuA_2. We have, in addition to equations (6) and (8),

$$b = [\mathrm{HA}] + [\mathrm{HB}], \text{ and } [\mathrm{HA}] = [\mathrm{CuAB}] + 2[\mathrm{CuB_2}], \text{ so that}$$
$$[\mathrm{CuAB}] = \sqrt{S_I(T - S_I)K_1/K_2 + (S_IK_1/2K_2)^2} - S_IK_1/2K_2.$$

From [CuAB] the other concentrations follow, and K_1 and K_2 can be calculated. Experiments carried out in the reverse direction, by making known additions of HA and saturating with CuB_2, lead in a similar way to values of K_3 and K_4, defined by the equations

$$K_3 = [\mathrm{CuAB}][\mathrm{HB}]/[\mathrm{CuB_2}][\mathrm{HA}] \quad . \quad . \quad (10a)$$
$$K_4 = [\mathrm{CuA_2}][\mathrm{HB}]/[\mathrm{CuAB}][\mathrm{HA}], \quad . \quad . \quad (10b)$$

K_3/K_4 being known, since $K_3/K_4 = K_1/K_2$.

It will be seen from equations (5a) and (10b) that K_4 should be the inverse of K_1, and since the determinations of these two constants are independent of one another, except that both depend on the value of S_M, this relation gives a valuable check on the validity of the equations and on the accuracy of the work. The results for acetyl acetone (HA) and benzoylacetone (HB) are given as an example :

Solid phase, CuA_2.		Solid phase, CuB_2.	
b (of HB).	K_1.	b (of HA).	K_3.
0·0110	2·07	0·0190	3·0
0·0239	1·96	0·0277	3·2
0·0294	1·98	0·0509	3·1
0·0367	2·01	0·0761	2·9
0·0640	2·05	0·1185	2·9
Mean K_1	2·0	Mean K_3	3·0
$\therefore K_2 =$	0·37	$K_4 =$	0·56

$$\therefore K_1K_4 = 1·1.$$

For another pair, dibenzoylmethane (HA) and benzoylacetone (HB), $K_1 = 3{\cdot}1$, $K_2 = 0{\cdot}46$; $K_3 = 2{\cdot}16$, $K_4 = 0{\cdot}32$, whence $K_1K_4 = 1{\cdot}01$. The differences between the values of K_1K_4 and unity are well within the effect of experimental error.

The possibility of this method of verification failed, however, when the equilibrium was very near either extreme, for in such cases one of the diketo-compounds reacts almost completely with the excess of the copper compound of the other, and its concentration is reduced to a value comparable with the experimental errors. In such a case, if the equilibrium is well over towards the side involving free HB, satisfactory constancy of K_1 and K_2 is found, but not of K_3 and K_4. The required verification must then be made by using the values of K_1 and K_2 to calculate the concentration of copper which should be reached in the addition of b of HA to excess of CuB_2, it being assumed that $K_1K_4 = K_2K_3 = 1$. This calculation involves an approximation method as follows :

In the equation

$$b = [HA] + [HB] = [HA] + [CuAB] + 2[CuA_2] \quad . \quad (11)$$

[HA] is, in the nature of the case, very small. As a first approximation $b = [HB] = [CuAB] + 2[CuA_2]$, which, with equation (6), leads to an approximate value of [CuAB]. From equation (10a) and $K_3 = 1/K_2$, it follows that an approximate value of [HA] can be calculated from

$$[HA] = K_2b\,[CuAB]/S_{II} \quad . \quad . \quad . \quad . \quad (12)$$

In the second approximation this value of [HA] is used in equation (11) and in the calculation of [CuAB], and $b - [HA]$ replaces b in equation (12). When successive approximations (3—5 are necessary) no longer cause a change in the value of [HA], this can be taken as correct, and all the other concentrations calculated from it. With acetylacetone [HA] and acetonedicarboxylic acid [HB], where the equilibrium is very much towards the side involving free HB, the numbers are :

Solid phase, CuA_2.

b (of HB).	T.	K_1.
0·0056	0·00408	0·030
0·0111	0·00455	0·041
0·0169	0·00468	0·032
0·0275	0·00506	0·032
0·0351	0·00535	0·035
	Mean K_1 =	0·034

$K_1/K_2 = 4{\cdot}6$, $\therefore K_2 = 0{\cdot}0074$.

Solid phase, CuB_2.

b (of HA).	T.	K_3.	T (calc. from $K_2 = 0{\cdot}0074$).
0·0140	0·0619	11·8	0·0618
0·0173	0·0667	—	0·0656
0·0209	0·0680	—	0·0690
0·0303	0·0760	70·6	0·0770

Thus the comparison of the results from the direct and the reverse reaction in this case is satisfactory even though the values of K_3 calculated directly vary so much.

In the summary of results on p. 2707, the methods of verification used and the divergencies found are quoted. Only in the case of benzoylacetone with acetoacetic ester are the divergences considerable, and the results, as a whole, give very strong support to our view of the mechanism of the reactions.

It is necessary to point out that, on this interpretation, some of the solutions in experiments involving the formation of very sparingly soluble copper compounds must be regarded as supersaturated after at least 48 hours' shaking; *e.g.*, in the case of acetylacetone with copper benzoylacetone as solid phase, the concentrations of copper acetylacetone ($S_I = 0{\cdot}00338$) in the last three experiments given on p. 2699 are 0·0040, 0·0070, and 0·0126. Since the value of S_M is 0·0879, and is unaffected by the presence of free HA or HB, while the values of T in these experiments are 0·0913, 0·1053, and 0·1260, it seems that in the absence of solid copper acetylacetone, its supersaturated solution, when it is so dilute, can remain in metastable equilibrium during the period of shaking. The constancy of K_3 and the proper relation of its value to that of K_2 (in the determination of which no difficulties of this kind occur) make this assumption necessary. In the additions of dibenzoylmethane to copper benzoylacetone, all the experiments resulted in solutions supersaturated with regard to copper dibenzoylmethane, even though the most concentrated was only 0·00114M. Here also the proper relations between the constants is found.

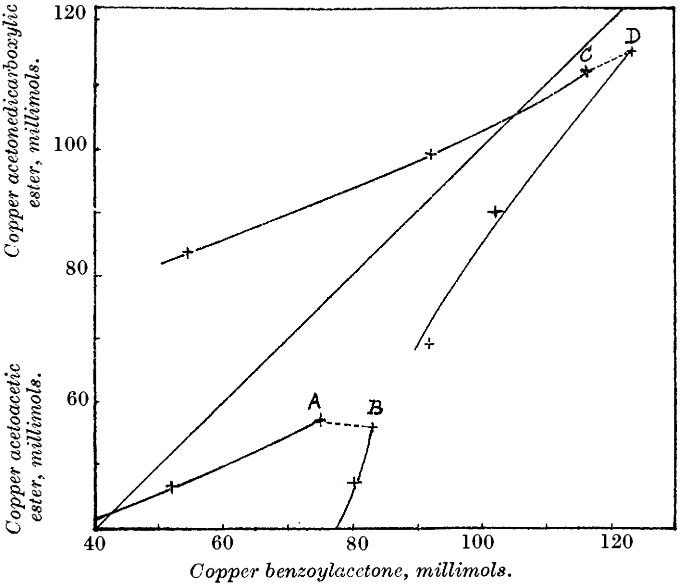
The Invariant Points.—In the cases where two invariant points occur (to which correspond copper concentration ${}_{I}S_M$ and ${}_{II}S_M$ for excess of CuA_2 and CuB_2 respectively), if the values of T found with known additions of CuA_2 in presence of excess of CuB_2 are plotted, the value of the addition necessary just to reach the point where T is identical with the value of ${}_{II}S_M$ can be read off the extrapolated curve. The difference between ${}_{II}S_M$ and this value of the addition of CuA_2 gives the amount of CuB_2 which must be dissolved to reach the invariant point, *i.e.*, to produce a saturated solution of CuAB, without causing precipitation of the latter. Since, further, the dissolved $CuB_2 = S_{II} + [CuAB]_2$, all the concentrations at an invariant point can be calculated.

Fig. 1 shows the upper parts of the curves for the two pairs of copper compounds which give two invariant points, obtained by plotting the amount of one compound dissolved against the additions of the other on rectangular axes. The broken curve AB represents the range of existence of CuAB as a solid when HA is benzoylacetone and HB is acetoacetic ester, and CD is the corresponding curve for the same HA and acetonedicarboxylic ester as HB. It will be noticed that neither intermediate compound can exist in equilibrium with its own solution.

The assumption that CuAB is the solid phase concerned has been tested in three ways :

(1) The value of [CuAB] at an invariant point, calculated as described above, is independent of any assumption other than that the solutions contain only CuA_2, CuB_2, and CuAB. These values are

Fig. 1.



	Point.	[CuAB].
Copper benzoylacetone ,, acetoacetic ester	A	0·058
	B	0·059
,, benzoylacetone ,, acetonedicarboxylic ester	C	0·127
	D	0·139

In both cases the pairs of values agree within the error of extrapolation, which supports the view that CuAB is a solid phase at the two invariant points.

(2) It follows from our equation that ${}_{\mathrm{I}}S_{\mathrm{M}} - {}_{\mathrm{II}}S_{\mathrm{M}} < S_{\mathrm{I}} - S_{\mathrm{II}}$ if CuAB is a solid phase. This relation is satisfied for the former pair, but not for the latter.

(3) From application of the arguments of Dimroth and Bamberger (*Annalen*, 1924, **438**, 67) to this case, it follows that G, defined by the equation $G = K_1 S_{\mathrm{I}} S_{\mathrm{II}} / K_2 (S_{\mathrm{CuAB}})^2$, must not be less than

unity if solid CuAB is to exist in contact with solution, and that G must be greater than $S_{\mathrm{I}}/S_{\mathrm{II}}$ (where $S_{\mathrm{I}}>S_{\mathrm{II}}$) if solid CuAB is to exist in contact with its own solution. For the first pair, $G = 1{\cdot}1$ and $S_{\mathrm{I}}/S_{\mathrm{II}} = 1{\cdot}90$, so the position of the curve AB is consistent with these relations. For the second pair, $G = 0{\cdot}62$ and $S_{\mathrm{I}}/S_{\mathrm{II}} = 1{\cdot}1$, according to which CuAB should not exist as a solid.

Thus, the assumption of CuAB as a solid at the two invariant points is verified for the first pair in every way by which it can be tested, while for the second pair two methods give adverse results. Other hypotheses examined were no more successful, and the discrepancy appears to be due to new effects—possibly purely physical—occurring at the abnormally high concentrations corresponding to the invariant points in this case, which will cause considerable departures from the ideal state assumed in deducing the equations.

No other part of the work is affected by this discrepancy.

Alcohol as Solvent.—Since the copper compounds of benzoylacetone (HA) and acetonedicarboxylic ester (HB) have smaller solubilities in alcohol, it appeared worth while to repeat the experiments in this solvent. This proved to be impossible because the solubility of $\mathrm{CuB_2}$ is depressed by addition of the ester HB ($S_{\mathrm{II}} = 0{\cdot}0229$ in alcohol; 0·0207 in presence of $0{\cdot}1363M$-HB, and 0·0206 in presence of $0{\cdot}2153M$-HB). In view of the isolation of alcoholates from the copper and nickel compounds of β-ketonic and *o*-hydroxy-esters (Wislicenus, *Ber.*, 1898, **31**, 3151; Doak and Packer, J., 1928, 2763), there can be little doubt that alcoholysis of this compound occurs and is suppressed by a small amount of ester. The results are consistent with the equation $K[\mathrm{EtOH}][\mathrm{CuB_2}] = \left[\mathrm{Cu}^{\mathrm{B}}_{\mathrm{OEt}}\right][\mathrm{HB}]$ if $K[\mathrm{EtOH}] = 2{\cdot}45 \times 10^{-4}$. According to this, the true solubility of $\mathrm{CuB_2}$ is 0·0206, and in the saturated solution approximately 10% has undergone alcoholysis. It was thus useless to carry out experiments with $\mathrm{CuB_2}$ as solid phase, but approximate values of K_1 and K_2 were obtained with $\mathrm{CuA_2}$ as solid.

Isolation of Intermediate Compounds.—Attempts to confirm the existence of intermediate compounds by determination of the freezing points of mixtures gave no decisive results on account of decomposition and the opacity of the liquids formed. But since Fig. 1 shows that the curves AB and CD are not far from the 45° line, it was possible that at a higher temperature they would cut it, in which case rapid crystallisation from hot benzene might allow of the preparation of the intermediate compounds.

Equivalent quantities of copper benzoylacetone and copper acetonedicarboxylic ester were dissolved in hot dry benzene, the solution rapidly cooled, and the dark green crystals kept in a vacuum

(Found : Cu, 14·93. $C_{19}H_{22}O_7Cu$ requires Cu, 14·93%). They melted at 121·5°, re-solidified and remelted at 127—128°. The product was next recrystallised quickly from hot alcohol, in which the solubilities of the two components are widely different, and the crystals were found to have the same copper content (14·99%) and to show the same behaviour as before on melting. A finely ground equimolecular mixture of the two components melts at 124°, with no temporary melt. Similar experiments with copper benzoylacetone and copper acetoacetic ester gave the results : Crystals from benzene (Found : Cu, 17·90. $C_{16}H_{18}O_5Cu$ requires Cu, 17·97%), m. p. 165—166°; recrystallised from alcohol, m. p. 165—166°; m. p. of equimolecular mixture of components 150°. Several similar experiments with copper benzoylacetone and copper dibenzoylmethane gave always the latter as the solid product. Thus, only in the two cases where it was found necessary to assume the existence of the intermediate *compound* as a solid phase were solids isolated which do not appear to be equimolecular mixtures and which have the required composition.

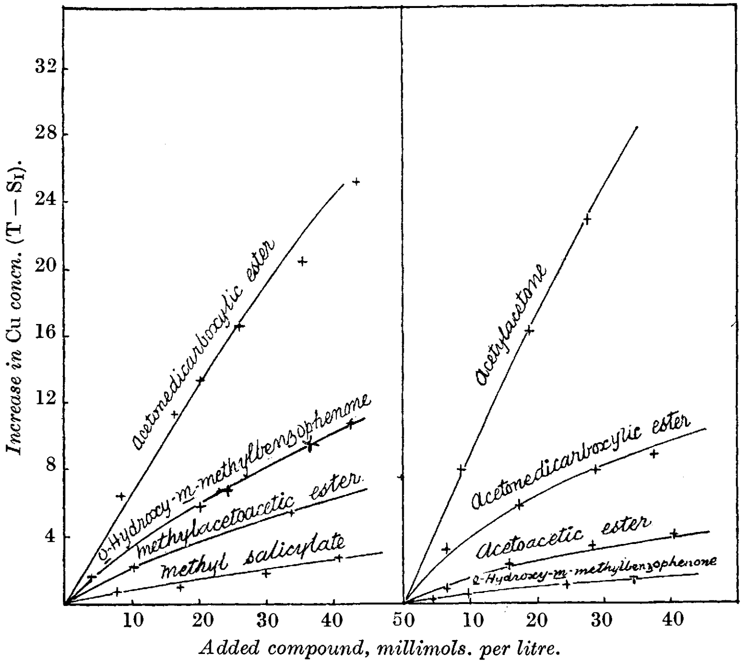
The collected values of K_1 and K_2 are :

A in CuA_2.	HB.	K_1.	K_2.	K_1/K_2.
COMe·CH·COMe	$Ph{\cdot}CO{\cdot}CH_2{\cdot}COMe$	2·0	0·37	5·4
,,	$CO(CH_2{\cdot}CO_2Et)_2$	0·034	0·0074	4·6
COPh·CH·COMe	$COMe{\cdot}CH_2{\cdot}COMe$	3·0	0·56	5·4
,,	$CO(CH_2{\cdot}CO_2Et)_2$	0·058	0·014	4·3
,,	,, (in EtOH)	0·053	0·010	5·3
,,	$CH_3{\cdot}CO{\cdot}CH_2{\cdot}CO_2Et$	0·0078	0·0031	2·5
,,	$CH_2(COPh)_2$	3·1	0·46	6·8
$CH(COPh)_2$	$COPh{\cdot}CH_2{\cdot}COMe$	2·2	0·32	6·8

From these values it appears that the co-ordinating affinity of the compounds decreases in the order : (1) dibenzoylmethane, (2) acetylacetone, (3) benzoylacetone, (4) acetonedicarboxylic ester, (5) acetoacetic ester, and that there is a large gap between (3) and (4).

To extend the comparison to compounds of which the pure copper derivatives could not be isolated (and for which, therefore, no values of the constants could be obtained) the increases of copper concentration produced by known additions of the compounds to systems containing one of the stable copper derivatives were determined and plotted. Fig. 2 shows the results with copper acetoacetic ester as solid phase for additions of *o*-hydroxy-*m*-methylbenzophenone, methylacetoacetic ester, and methyl salicylate in comparison with those for acetonedicarboxylic ester. With copper benzoylacetone as solid phase (Fig. 3), methylacetoacetic ester and methyl salicylate produce effects too small for plotting, but the curves for all the substances are in the same order as in Fig. 2. *o*-Hydroxy-*m*-methylacetophenone gives a curve identical with that for the corresponding benzophenone, and ethyl malonate and salol were found to have no measurable effect. The order of co-ordinating affinity may thus be continued after acetoacetic ester: (6) *o*-hydroxy-*m*-methylbenzophenone and the corresponding acetophenone, (7) methylacetoacetic ester, and (8) ethyl malonate and salol giving a zero value. It is of considerable interest that this order is almost the same as that found by K. H. Meyer (*Annalen*, 1911, **380**, 242) for the percentage of enol form in the pure substances, *viz.*, dibenzoylmethane 102, benzoylacetone 99, acetylacetone 80·4, acetonedicarboxylic ester 16·8, acetoacetic ester 7·4, and methylacetoacetic ester 4·1. This parallelism is a strong confirmation of Sidgwick's view (" Electronic Theory of Valency," p. 147) that the enol forms of β-diketo-compounds are chelated. Both lists also show the great difference between the effect of a true ketone group and of a carboxylic —CO— group, and our figures indicate that symmetry is a favourable factor in chelation. It is of interest, too, that methyl salicylate and the simple *o*-hydroxy-aromatic ketones should be so low on the list in view of the apparent

FIG. 2. FIG. 3.



Solid phase, copper acetoacetic ester.

Solid phase, copper benzoylacetone.

stability of the lakes formed by mordanting dyes derived from salicylic acid and 1-hydroxyanthraquinone.

The value of K_1/K_2 is the greater the higher the concentration of CuAB in presence of standard concentrations of CuA_2 and CuB_2. But with one of the sparingly soluble copper compounds as CuA_2 or CuB_2, the concentration of CuAB must remain small even with the higher values of K_1/K_2, and accordingly all the cases involving either copper acetylacetone or copper benzoylacetone give only one invariant point. The tendency to form the intermediate compound, as measured by K_1/K_2, is actually least in those cases where it has been necessary to assume its existence as a solid, the diminution in K_1/K_2 being more than compensated by the higher solubility of CuA_2 or CuB_2 so that comparatively large concentrations of CuAB are reached, and saturation results.

EXPERIMENTAL.

Materials were purified by standard methods until their b. p.'s or f. p.'s agreed with those in the literature. All transferences of material, including collection of distillates, were carried out in dry air. In the purification of the Cu derivatives, the prevention of decomp. by traces of H_2O is the most important point. Dry EtOH was used wherever possible for recrystn., since traces of H_2O present despite the precautions, had less effect in this solvent than any other. In this respect C_6H_6 is particularly unsuitable, a qualitative confirmation of Greer's results (*J. Amer. Chem. Soc.*, 1930, **52**, 4191) on the activity of H_2O in C_6H_6. Cu acetylacetone is best recryst. from $CHCl_3$–EtOH; Cu dibenzoylmethane is not sufficiently sol. for recrystn., but, when prep. from $Cu(OAc)_2$ and very slight excess of the diketone in dry EtOH, and repeatedly washed with EtOH, it was found to be pure. The Cu derivatives were prepared in small quantities and each prepn. was analysed separately.

Estimation of Cu was by titration of the I liberated from KI in presence of AcOH, with $N/100$-$Na_2S_2O_3$ stabilised by Na_2CO_3. No difficulty was experienced with the dil. $Na_2S_2O_3$ so long as the vol. of solution did not exceed 100 c.c. and an atm. of N was maintained in the titration vessel. Comparative expts. showed that this method agreed with the gravimetric method by Cu_2S and that the presence of the keto-esters and C_6H_6 had no effect. With diketones, complete reaction of the Cu compounds is reached only after addition of C_6H_6 and shaking. The $N/100$-$Na_2S_2O_3$ was restandardised each day against electrolytic Cu, but showed no variation.

For determination of solubility, a shaking bottle containing the solid was kept over P_2O_5 in vac. for at least 24 hrs., and then attached to an apparatus by which C_6H_6 could be distilled directly into the bottle through dry air, after rejection of 20 c.c. The stoppers were covered with thin rubber caps fitting tightly round the necks of the bottles, and further sealed by collodion. The bottles were fixed in cages which prevented any motion of the stoppers. Preliminary expts. starting from higher and lower temps. showed that equil. was reached after 24 hrs. in the thermostat; but shaking was continued for not less than 48 hrs. Filtration was carried out in the thermostat, dry air passed over C_6H_6 at 25° being used to force the liquid first through coarse filter-paper and then through cotton-wool. Either material alone was unsatisfactory, the paper letting fine particles through, and the cotton-wool becoming choked unless the liquid was almost clear. Volumes varying according to Cu content of solution were measured out for analysis with narrow-necked pipettes, at least two titrations being made for each bottle. With some of the more conc. solutions, titration was begun with $N/10$-$Na_2S_2O_3$ by wt. and finished with $N/100$-$Na_2S_2O_3$.

To exclude moisture in the prepn. of solutions containing known amounts of diketo-compounds or of Cu derivatives, two slightly upward-sloping tubes were fused on to opposite sides of the neck of a graduated flask, one high up and the other sufficiently above the bulb of the flask to allow of 10 graduations, 1 mm. apart. Into this flask containing the weighed substance, C_6H_6 was distilled as described above until the graduations were reached, and the vol. of solution at 25° determined. The solution was transferred to a shaking bottle containing the solid phase in use through the lower tube, air entering through a P_2O_5 tube attached to the upper side tube. In cases where the amount of Cu derivative to be added would not dissolve in the vol. of C_6H_6 to be used, it was weighed directly into the shaking bottle, and the measured vol. of C_6H_6 added in the same way.

Results.

Molecular-weight Determination (*cryoscopic in* C_6H_6).—Cu acetoacetic ester 325 (calc., 322); Cu acetonedicarboxylic ester 471, 474 (calc., 466); Cu benzoylacetone 370 (calc., 386).

Solubilities (*mols./litre*).—(1) *In* C_6H_6 *at* 25°.

Cu acetylacetone	0·00338	(6 values, 0·00336—0·00339).
,, benzoylacetone	0·0533	(6 values, 0·0531—0·0534).
,, dibenzoylmethane	0·00040	(2 identical values).
,, acetonedicarboxylic ester	0·0484	(6 values, 0·0477—0·0487).
,, acetoacetic ester	0·0280	(6 values, 0·0278—0·0283).
(2) *In* EtOH *at* 25°.		
,, benzoylacetone	0·00485	
,, acetonedicarboxylic ester	0·0229	(see p. 2703).

Equilibria in Benzene at 25°.

Benzoylacetone (HA) *and acetylacetone* (HB).

$S_M = 0·0879$ (5 values, 0·0878—0·0880); $K_1/K_2 = 5·4$ (from S_M), 5·3 (from addn. of CuA_2 to CuB_2).

HB with CuA_2, $K_1 = 3·0$ (5 values, 2·9—3·2), $K_2 = 0·56$.

HA with CuB_2, $K_3 = 2·0$ (6 values, 1·9—2·1), $K_4 = 0·37$.

Benzoylacetone (HA) *and dibenzoylmethane* (HB).

$S_M = 0·0657$ (3 values, 0·0656—0·0658); $K_1/K_2 = 6·8$ (from S_M).

HA with CuB_2, $K_3 = 2·2$ (6 values, 1·98—2·29), $K_4 = 0·318$.

HB with CuA_2 $\begin{cases} K_1 = 3·1 \text{ (3 values, 2·7—3·5), } K_2 = 0·46. \\ \text{Verification of } T\text{, using } K_3 = 2·2\text{, gave av. error 0·3\% and} \\ \quad \text{max. error 1\%.} \end{cases}$

Acetylacetone (HA) *and acetonedicarboxylic ester* (HB).

$S_M = 0·0794$ (4 values, 0·0784—0·0805); $K_1/K_2 = 4·6$ (from S_M), 4·3 (from addn. of CuB_2 to CuA_2).

Verification of T, using $K_1/K_2 = 4·6$: (i) for addn. of CuB_2 to CuA_2, av. error 0·5%, max. error 1·3%; (ii) for converse addn., av. error 2·8%, max. error 3·6%.

HB with CuA_2, see p. 2698.

HA with CuB_2, see p. 2698.

Benzoylacetone (HA) *and acetonedicarboxylic ester* (HB).
$_{\mathrm{I}}S_{\mathrm{M}}$ = 0·239 (3 values, 0·238—0·240), $_{\mathrm{II}}S_{\mathrm{M}}$ = 0·228 (3 values, 0·227—0·229); K_1/K_2 = 4·3 from smooth curves for addn. of CuA_2 to CuB_2 and *vice versa.*
Verification of T, using K_1/K_2 = 4·3 : (i) addn. of CuB_2 to CuA_2, av. error 0·6%, max. error 2%; (ii) reverse addn., av. error 0·1%, max. error 3%.
To reach invariant point D (Fig. 1), 0·116 mol./l. CuB_2 required; to reach invariant point C (Fig. 1), 0·116 mol./l. CuA_2 required.
HB with CuA_2, K_1 = 0·058 (5 values, 0·055—0·062), K_2 = 0·0135.
HA with CuB_2, verification of T, using K_1 = 0·058, av. error 0·5%, max. error 2%.
Benzoylacetone (HA) *and acetoacetic ester* (HB).
$_{\mathrm{I}}S_{\mathrm{M}}$ = 0·139 (2 identical values), $_{\mathrm{II}}S_{\mathrm{M}}$ = 0·132 (3 values, 0·130—0·134); K_1/K_2 = 2·5 from smooth curves for addn. of CuB_2 to CuA_2.
Verification of T, using K_1/K_2 = 2·5, addn. of CuB_2 to CuA_2, av. error 0·6%, max. error 3·9%.
To reach invariant point B (Fig. 1), 0·056 mol./l. CuB_2 required.
To reach invariant point A (Fig. 1), 0·075 mol./l. CuA_2 required.
HB with CuA_2, K_1 = 0·0078 (4 values, 0·0070—0·0086), K_2 = 0·0031.
HA with CuB_2, verification of T, using K_1 = 0·0078, av. error 2·3%, max. error 4·8%.
Equilibria in Alcohol at 25°.
Benzoylacetone (HA) *and acetonedicarboxylic ester* (HB).
$_{\mathrm{I}}S_{\mathrm{M}}$ = 0·0458 (3 values, 0·0457—0·0459), $_{\mathrm{II}}S_{\mathrm{M}}$ = 0·0463 (2 identical values); K_1/K_2 = 5·4 (3 values, 5·1—5·9) from addn. of CuB_2 to CuA_2.
HB with CuA_2, K_1 = 0·053 (3 values, 0·049—0·055); K_2 = 0·01.

SUMMARY.

β-Diketo-compounds react rapidly (in some cases instantaneously) with the copper derivatives of other diketo-compounds, producing equilibria $CuA_2 + HB \rightleftharpoons CuAB + HA$ and $CuAB + HB \rightleftharpoons CuB_2 + HA$. The copper derivatives themselves react, producing the equilibrium $CuA_2 + CuB_2 \rightleftharpoons 2CuAB$. For each pair of diketo-compounds examined, as many as possible of the following series of determinations have been carried out with benzene as solvent at 25°, and for one pair in alcoholic solution : (*a*) composition of the solution at the invariant point (or points) reached with two solid phases present; (*b*) composition of solutions produced by addition of known amounts of CuA_2 in presence of excess of CuB_2; (*c*) the reverse of (*b*); (*d*) composition of solutions produced by addition of known amounts of HB in presence of excess of CuA_2; (*e*) the reverse of (*d*). It has been shown that, except for a region of comparatively high concentration in one case, all the results are quantitatively consistent with the above three equations. In two cases (HA = benzoylacetone and HB = either acetonedicarboxylic ester or acetoacetic ester) solid CuAB can exist in contact with solutions containing an excess of CuA_2.

The values obtained for the equilibrium constants corresponding to the equations indicate that the co-ordinating affinity of the

β-diketo-compounds in their copper derivatives follows the same order as the percentage of enol contained in the pure compounds. No evidence was found for the existence of compounds, such as CuA_2,HB, containing 6-covalent copper.

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