208. *The Reaction of Malonic Acids with Metallic Bases.*

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Ives and Riley (J., 1931, 1998) have prepared a number of metal malonates and measured the conductivities of their clear aqueous solutions, but Britton and Jarrett (this vol., p. 168) have raised the question: how can a base such as copper hydroxide, which is ordinarily precipitated from aqueous solutions at $p_H = 5{\cdot}3$, yield with an acid as weak as malonic acid a normal soluble salt? A 0·04*M*-sodium malonate solution, as they point out, has a p_H value of 9·06. They answer the question, on the basis of new p_H and conductivity measurements, by supposing that very extensive hydrolysis exists according to the scheme: $2H_2O + 2CuM \rightleftharpoons Cu(HM)_2 + Cu(OH)_2$, the hydrogen malonate then hydrolysing still further: $Cu(HM)_2 + 2xH_2O = xCu(OH)_2 + (1 - x)Cu(HM)_2 + 2xH_2M$. Some of the copper hydroxide, they assume, is associated in solution with the hydrogen malonate, forming basic aggregates which are maintained in solution in a highly dispersed state.

These hypotheses seemed unnecessary, and since they will affect work now in progress, the available data have been re-examined. Copper malonate has been shown by Riley and Ives (J., 1930, 1642; *loc. cit.*) to be a weak salt, and one with a strong tendency to form complex anions. The dissociation constants for the processes $CuM \rightleftharpoons Cu^{\cdot\cdot} + M''$ and $CuM_2'' \rightleftharpoons CuM + M''$ have been found to be $2{\cdot}5 \times 10^{-6}$ and $2{\cdot}8 \times 10^{-3}$ respectively (Davies, "Conductivity of Solutions," 1933, pp. 110, 190). The following table shows some of the figures that were derived in calculating these values; col. 1 gives the total concentration in millimoles per litre, and cols. 2—5 give, in the same units, the concentrations of the malonate ion, undissociated copper malonate, the complex anion, and copper ion. Col. 6 shows $-\log m_{Cu}$, calculated from col. 5, and col. 7 gives p_{Cu} as measured by Britton and Jarrett. The agreement between these last two columns shows that the high p_{Cu} values are fully explained by the weakness of the salt.

m.	$m_{M''}$.	m_{CuM}.	$m_{CuM_2''}$.	$m_{Cu^{\cdot\cdot}}$.	$-\log m_{Cu}$ (calc.).	p_{Cu} (obs.).
20	0·099	18·52	0·690	0·789	3·10	3·07
10	0·087	9·314	0·300	0·387	3·41	3·38
5	0·077	4·680	0·122	0·199	3·70	3·59

In these calculations no allowance was made for hydrolysis, but the figures provide a basis on which this correction can be made. Taking the second dissociation constant of malonic acid as $K = 4{\cdot}4 \times 10^{-6}$ (Britton, J., 1925, **127**, 1909), and representing the reaction of the copper ion as $Cu^{\cdot\cdot} + OH' \rightleftharpoons CuOH^{\cdot}$, we can calculate from Britton and Jarrett's measurement, $p_H = 5{\cdot}54$, that in the $0{\cdot}02M$-solution the ions HM' and $CuOH^{\cdot}$ are present at an approximate concentration 6×10^{-5} g.-mol./l.; the concentrations of the other ions are hardly changed from the values shown in the table, owing to the large proportion of undissociated salt available. The effect of this hydrolysis on the conductivity of the salt is very small, being comparable with the ordinary solvent correction, so that there is no reason to doubt the validity of the calculations, and no reason for assuming the presence of copper hydroxide in appreciable amounts. A further point of interest in the calculations is that they provide the necessary data for estimating the strength of copper hydroxide; for the process $CuOH^{\cdot} \rightleftharpoons Cu^{\cdot\cdot} + OH'$, the figures already quoted lead to the approximate value $K = [Cu^{\cdot\cdot}][OH']/[CuOH^{\cdot}] = 3 \times 10^{-8}$. Copper hydroxide is therefore a weaker electrolyte than malonic acid, and this accounts for the low p_H values found by Britton and Jarrett for copper malonate solutions. If the reaction of the copper ion is written in the form: $Cu^{\cdot\cdot},6H_2O \rightleftharpoons CuOH,5H_2O^{\cdot} + H^{\cdot}$, the acid dissociation constant of the cupric ion becomes $K_a = 3 \times 10^{-7}$.

Britton and Jarrett have also studied copper hydrogen malonate solutions. The composition of such solutions can be calculated, for it can easily be shown that the amounts of $CuOH^{\cdot}$ and CuM_2'' present are small enough to be neglected, so that the six species to be estimated are H_2M, HM', M'', $Cu^{\cdot\cdot}$, CuM and $H^{\cdot}$, and to determine these we have six equations, given by the first and second dissociation constants of malonic acid, the dissociation constant of copper malonate, and the following: $[H^{\cdot}] + [HM'] + 2[H_2M] = 1/v$, $[Cu^{\cdot\cdot}] + [CuM] = 1/2v$, and $2[Cu^{\cdot\cdot}] + [H^{\cdot}] = [HM'] + 2[M'']$ for electroneutrality. Solution by successive approximations for $v = 800$ gives $p_H = 3{\cdot}45$, $p_{Cu} = 3{\cdot}79$, and $\Delta = 134$. The measured values of Britton and Jarrett are respectively 3·57, 3·44, and 120. The agreement is not exact, and this is partly due to the inevitable approximations in the calculations; the conductivity, for instance, is reckoned from mobilities at infinite dilution, and activity corrections are neglected throughout. Nevertheless, the agreement is sufficiently close to show that the low p_H and high p_{Cu} values, and the high conductivity, do not demand extensive hydrolysis for their explanation; they are primarily due to the weakness of copper malonate, the main reaction being expressed by the equation: $Cu^{\cdot\cdot} + HM' \rightleftharpoons CuM + H^{\cdot}$.

With zinc and magnesium malonates Britton and Jarrett find smaller anomalies, and this is in agreement with the greater dissociation constants of these salts. It can be concluded that, although some hydrolysis does occur in solutions of all these salts, yet the amount of metal hydroxide produced never exceeds the minute quantities that can be maintained in true solution.

These conclusions do not apply to all of the substituted malonates studied by Riley and Ives. According to Gane and Ingold (J., 1929, 1698), the second dissociation constants of diethyl- and di-*n*-propyl-malonic acids are respectively $5{\cdot}9 \times 10^{-8}$ and $3{\cdot}4 \times 10^{-8}$, values approximately 100 times smaller than that of malonic acid itself. Furthermore, as will be shown, the tendency to form undissociated molecules and complex anions is several hundred times smaller for these salts than for copper malonate. Both factors, the weakness of the acid and the greater dissociation of the salt, markedly favour hydrolysis, and it is probable that in the highly dilute solutions studied by Ives and Riley ($m < 0{\cdot}0005$) the disubstituted salts are so extensively hydrolysed as to render the conductivity results an unreliable guide to their strength. This opinion is confirmed on examining Riley's potentiometric data (J., 1930, 1642); he found abnormal results for the electrometric titration of $0{\cdot}01M$-copper sulphate with sodium diethyl- or dipropyl-malonate. On the first addition of the malonate solution, there is a fall in potential corresponding to an increase in copper-ion activity; this was attributed to the greater dissociation of the copper malonate as compared with copper sulphate, but this must be erroneous, for the sulphate-ion concentration was maintained constant at $0{\cdot}01M$, and the suggested effect could not occur. On further additions there is a region (extending up to a malonate concentration of $0{\cdot}02M$) in which the solutions are turbid and the potentials not reproducible, and there can be little doubt that hydrolysis is indeed considerable in these solutions. At higher concentrations of the sodium disubstituted malonates the solutions become clear. The potentials are now reproducible, but they are quite incompatible with the dissociation constant $K = [Cu^{\bullet\bullet}][X'']/[CuX] = 4 \times 10^{-6}$ derived by Ives and Riley for these two salts (their recorded values, which are twice as great, were calculated from g.-equivs.). For instance, taking the last row of figures in Riley's table, we have: total concentration of sodium dipropylmalonate = 0·1 g.-mol., total concentration of copper sulphate = 0·01 g.-mol., and $[Cu^{\bullet\bullet}] = 5{\cdot}81 \times 10^{-5}$. Hence $[X'']/[CuX] = K/5{\cdot}81 \times 10^{-5}$, and since $[X'']$ cannot be much less than 0·08 (the value it would have if the sodium salt were strong, but all the copper were present as CuX_2''), and $[CuX]$ cannot be as great as 0·01, it follows that K cannot be less than 4×10^{-4}, and may be much greater. Separate lines of evidence therefore indicate that copper diethyl- and dipropyl-malonates are extensively hydrolysed, and that conductivity measurements give results of the wrong order of magnitude for the dissociation constants of these salts.

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