

347. A Cryoscopic Study of Trichloroacetic Acid and its Hydrate in Benzene and in Dioxan Solution.

By R. P. BELL and M. H. M. ARNOLD.

It has been previously shown (Bell, *Z. physikal. Chem.*, 1930, **150**, A, 20) that a solution of trichloroacetic acid in benzene will take up water to form a stable monohydrate. The acid itself is known to exist chiefly as double molecules in benzene, and it is of interest to discover whether the hydrate has the formula, $\text{CCl}_3\cdot\text{CO}_2\text{H}\cdot\text{H}_2\text{O}$, 1 mol. of water replacing one of acid, or whether double molecules $(\text{CCl}_3\cdot\text{CO}_2\text{H})_2\cdot 2\text{H}_2\text{O}$ are formed. The structure of the double molecules of trichloroacetic acid itself has recently received a satisfactory explanation (see Sidgwick, *Ann. Reports*, 1934, **31**, 40), and it may be hoped that hydrate formation can be accounted for on similar lines.

This point can be investigated by freezing-point measurements, which have already been employed by Meisenheimer (*Annalen*, 1930, **482**, 130) for detecting cross association between hydrogen chloride and hydroxy-compounds in nitrobenzene and dioxan. In the present investigation, measurements were carried out with benzene solutions of dry trichloroacetic acid and of its equimolecular mixture with water, the equilibrium method previously described (Bell, Baughan, and Vaughan-Jackson, *J.*, 1934, 1969) being used. The trichloroacetic acid was a pure product dried over phosphoric oxide, and the benzene was specially purified for freezing-point determinations, dried over phosphoric oxide, and distilled before use. The samples of solution withdrawn were analysed by titration with baryta. The results obtained are given in the following tables, in which m = mols. of acid per 1000 g. of solvent, and ΔT = freezing-point depression.

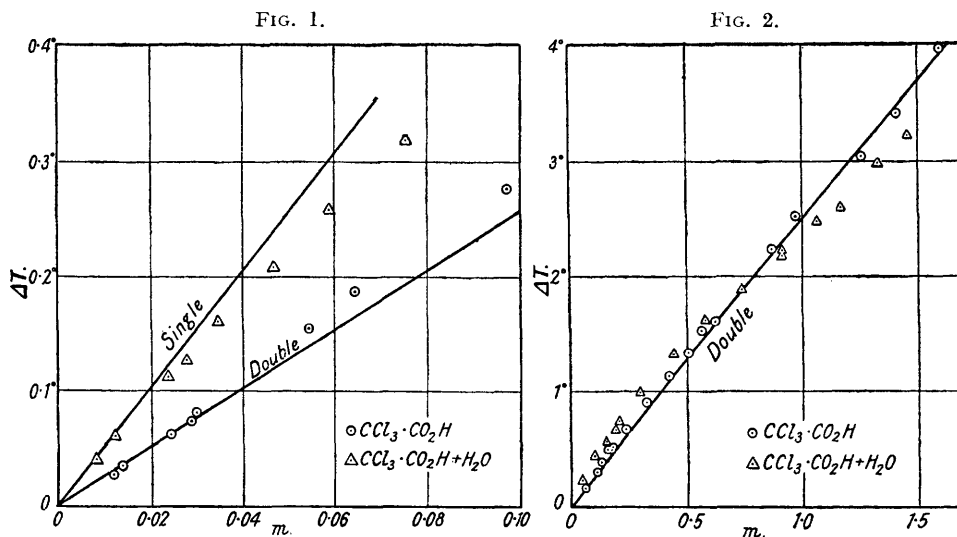
<i>Trichloroacetic acid in benzene.</i>						<i>Trichloroacetic acid and water in benzene.</i>					
<i>m.</i>	$\Delta T.$	<i>m.</i>	$\Delta T.$	<i>m.</i>	$\Delta T.$	<i>m.</i>	$\Delta T.$	<i>m.</i>	$\Delta T.$	<i>m.</i>	$\Delta T.$
0.0119	0.031°	0.106 ₀	0.293°	0.505	1.333°	0.0082	0.040°	0.0828	0.341°	0.743	1.880°
0.0140	0.035	0.125 ₅	0.333	0.566	1.533	0.0123	0.061	0.106	0.425	0.913	2.180
0.0245	0.061	0.152 ₅	0.486	0.623	1.605	0.0236	0.112	0.153	0.540	0.918	0.207
0.0288	0.073	0.171 ₂	0.480	0.876	2.230	0.0277	0.127	0.192	0.676	1.065	2.476
0.0301	0.081	0.177	0.510	0.974	2.510	0.0345	0.161	0.203	0.727	1.170	2.594
0.0542	0.155	0.232	0.663	1.261	3.032	0.0468	0.208	0.298	0.988	1.360	2.981
0.0644	0.187	0.324	0.902	1.410	3.405	0.0590	0.259	0.447	1.320	1.565	3.437
0.0972	0.276	0.424	1.133	1.600	3.975	0.0752	0.319	0.590	1.610		

The results of these cryoscopic measurements can only be interpreted simply if the solid phase throughout is pure benzene. To test this point, measurements were carried out by the method of van Bijlert (*Z. physikal. Chem.*, 1891, **8**, 343) with carbon tetrachloride as a reference substance. The samples of liquid and mush were analysed by titrating one portion with alkali and determining the density of another portion (after removal of acid and water). Successive experiments with dry trichloroacetic acid gave the values 5%, (– 6%, – 1%), 5%, 8%, 10%, 14%, 9%, 8%, 4% for the partition coefficient of trichloroacetic acid between the solid and the liquid phase. The mean of these values is 6%, with a probable error of $\pm 2\%$. Similar experiments with an equimolecular mixture of trichloroacetic acid and water gave the same value within the experimental error. Similar results were obtained by Bury and Jenkins (*J.*, 1934, 688) for the system acetic acid–benzene. They attributed the presence of acid in the solid phase to adsorption, which

seems the most probable explanation in the present case, especially in view of the erratic nature of the results. Even if there is actually a small degree of mixed-crystal formation, it is not enough to invalidate a qualitative interpretation of the results, and will certainly permit a comparison between the wet and the dry solutions.

The cryoscopic results for the dilute solutions are shown in Fig. 1, and the whole range of concentrations in Fig. 2 (in which the points for the dilute range are omitted for the sake of clarity). The theoretical lines for single and double molecules are based on the equation, $\Delta T = 5.122m - 0.261m^2$, given by Bury and Jenkins (*loc. cit.*) for an ideal solute.

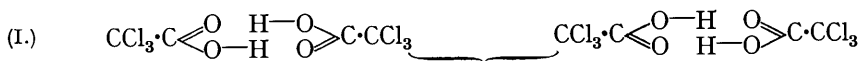
In the case of the dry acid, the points lie close to the theoretical line for double molecules over the whole range of concentrations. There is a slight but definite tendency for the points to lie above the line in the middle concentration range. It does not seem possible to account for this by assuming a small dissociation of the double molecules into single molecules, because the deviations disappear at the lowest concentrations instead of becoming greater. The deviations may well be due to the same complex physical causes which lead to "positive" deviations from ideal behaviour in the vapour-pressure curves of many binary liquid mixtures.



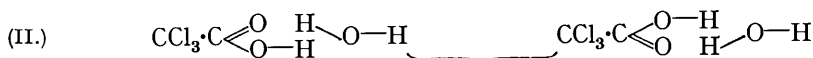
The most direct information about the solutions containing water is afforded by the results in dilute solution. It is seen at once that in very dilute solution the hydrate gives a f.-p. depression exactly twice as great as the dry acid, *i.e.*, the molecules present must be $\text{CCl}_3 \cdot \text{CO}_2\text{H}, \text{H}_2\text{O}$ and not $(\text{CCl}_3 \cdot \text{CO}_2\text{H})_2, 2\text{H}_2\text{O}$. As the concentration increases, the data for the wet solutions indicate a gradually increasing association, and at a concentration of about $m = 0.7$ the f.p.'s of the wet and the dry solution are the same, which would correspond to complete association of $\text{CCl}_3 \cdot \text{CO}_2\text{H}, \text{H}_2\text{O}$ to $(\text{CCl}_3 \cdot \text{CO}_2\text{H})_2, 2\text{H}_2\text{O}$. The experimental results do not provide conclusive evidence for the existence of double hydrated molecules, for at higher concentrations the apparent association is somewhat greater than 2. However, the shape of the curve differs from the type usually found for "continuous" association (*e.g.*, alcohol in benzene, where the association is probably due to a purely physical interaction) in that it falls off rapidly at first but much more slowly after passing the theoretical curve for double molecules. The apparent increase of the degree of association to slightly more than 2 may well be due to physical interaction at the high concentrations involved. The existence of the molecule $(\text{CCl}_3 \cdot \text{CO}_2\text{H})_2, 2\text{H}_2\text{O}$ thus appears probable, though it is much less stable than the $(\text{CCl}_3 \cdot \text{CO}_2\text{H})_2$ molecule, being roughly 50% dissociated into $\text{CCl}_3 \cdot \text{CO}_2\text{H}, \text{H}_2\text{O}$ at $m = 0.15$.

The only satisfactory structure for the double molecules of carboxylic acids is that proposed by Sidgwick (*loc. cit.*), in which the older conception of doubly covalent hydrogen

is interpreted as a resonance state between two "classical" structures, *e.g.*, in the present case (I). A feasible structure for the single hydrate molecule can be written by replacing



one acid molecule by a water molecule, *i.e.*, (II). This is not, however, the only possible structure. For instance, by analogy with chloral hydrate, $\text{CCl}_3 \cdot \text{CH}(\text{OH})_2$, we may write

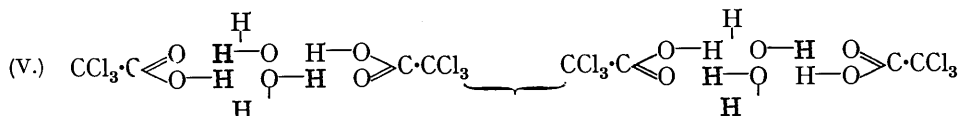


(III), though this formula has the disadvantage of assuming that three hydroxyl groups are attached to one carbon atom.*

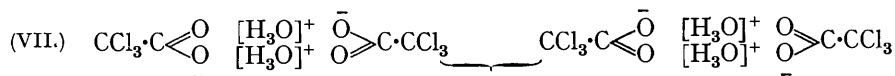


By analogy with the crystal structure of perchloric acid hydrate, $[\text{H}_3\text{O}]^+[\text{ClO}_4]^-$, a further possible structure is (IV), which is supported to a certain extent by the fact that the formation of a hydrate appears to be related to the acid strength; thus tri-, di-, and monochloroacetic and acetic acids form hydrates to an extent which decreases in the order given (Bell, *Z. physikal. Chem.*, 1930, **150**, A, 20), and the strong acid hydrochloric acid associates considerably with water and alcohols when dissolved in nitrobenzene or dioxan (Meisenheimer, *loc. cit.*).

A similar ambiguity is encountered in attempting to assign a structure to the double molecule $(\text{CCl}_3 \cdot \text{CO}_2\text{H})_2 \cdot 2\text{H}_2\text{O}$. By analogy with (I) and (II) we can write a resonance structure (V), though it may be remarked that this could be logically extended to include



any number of water molecules, whereas actually an exactly equivalent amount of water is taken up (Bell, *ibid.*). Structure (IV) might form a double dipole aggregate, as in (VI), but can also give rise to a resonance structure for the double molecules, (VII), and in this case the hydration must stop at 1 mol. of water per mol. of acid. The free charges in this structure might lead to an apparent degree of association greater than 2. Structure (III)



would not be expected to form double molecules, but would exhibit continuous association like the alcohols. As for the single hydrate molecules, there is insufficient evidence to discriminate with certainty between the alternative structures.

It was thought of interest to investigate hydrate formation in a solvent in which carboxylic acids are present chiefly as single molecules. From the very meagre data available, this appears to be the case in solvents containing oxygen, and measurements were therefore carried out in dioxan (diethylene dioxide).

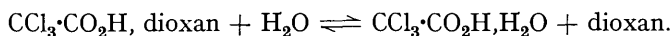
The dioxan was purified by freezing and dried over sodium; m. p. 11.8° . The cryoscopic technique was exactly the same as for benzene. The following results were obtained for solutions of trichloroacetic acid and of its equimolecular mixture with water.

* Unpublished experiments show that dry trichloroacetic acid is about four times as efficient a catalyst as the hydrate for the rearrangement of *N*-bromoacetanilide in benzene solution (cf. Bell, *Proc. Roy. Soc.*, 1934, **143**, 377; Bell and Levinge, *ibid.*, 1935, **151**, 211). This is evidence against the structure $\text{CCl}_3 \cdot \text{C}(\text{OH})_3$, which would presumably be a very weak acid relative to trichloroacetic acid.

Trichloroacetic acid in dioxan.				Trichloroacetic acid + water in dioxan.			
<i>m.</i>	$\Delta T.$	<i>m.</i>	$\Delta T.$	<i>m.</i>	$\Delta T.$	<i>m.</i>	$\Delta T.$
0.0462	0.195°	0.411	1.910°	0.488	2.340°	0.0387	0.248°
0.148	0.625	0.426	2.035	0.539	2.520	0.121	0.736
0.196	0.922	0.498	2.319	0.557	2.648	0.287	1.641
0.346	1.535					0.393	2.131°
						0.523	2.858

The results are shown graphically in Fig. 3. The full line is the theoretical curve for single-acid molecules forming an ideal solution, based on the results of Bell and Wolfenden (this vol., p. 822) for the normal solute chlorobenzene. The points for dry trichloroacetic acid are seen to fall well on this line, showing that the acid is present entirely as single molecules. This contrasts strongly with the results in benzene (having practically the same dielectric constant) and in *p*-chlorotoluene (having a considerably greater dielectric constant), in both of which only double molecules are present (cf. Bell, Baughan, and Vaughan-Jackson, *loc. cit.*). It is evident that (as for electrolytic dissociation) the chemical type of the solvent is one of the most important factors in determining the degree of association. The acid molecules are probably unable to combine with one another in dioxan because they are already combined with the oxygen atoms of the solvent molecules. The work of Weissberger and Högen (*Z. physikal. Chem.*, 1931, 156, A, 321) and Weissberger and Fasold (*ibid.*, 1931, 157, 65) shows that trichloroacetic acid forms compounds with a large number of oxygen compounds in hexane solution.

The broken line in the figure is obtained by addition from the results for dry acid alone and the results for water alone (the latter taken from the data of Bell and Wolfenden, *loc. cit.*): it thus represents the f. p. depressions which would be obtained with the mixture, $\text{CCl}_3\cdot\text{CO}_2\text{H} + \text{H}_2\text{O}$, in the absence of any interaction between the components. The actual results lie very much lower, and are consistent with the incomplete formation of a hydrate $\text{CCl}_3\cdot\text{CO}_2\text{H}\cdot\text{H}_2\text{O}$ by the equilibrium



SUMMARY.

(1) Cryoscopic measurements have been carried out with solutions of trichloroacetic acid and its hydrate in benzene. A phase-rule study shows that the solid phase contains a little trichloroacetic acid (probably in an adsorbed state) but not enough to interfere with a simple interpretation of the results.

(2) The dry acid is present in benzene solution essentially as double molecules over the whole concentration range investigated ($m = 0.01$ — 1.5). The hydrate is present entirely as single molecules in dilute solutions, and probably forms double molecules at higher concentrations. A number of different structures have been proposed for the single and the double hydrate molecule.

(3) Similar measurements have been carried out with dioxan solutions. Trichloroacetic acid is present entirely as single molecules in this solvent, probably because it is associated with solvent molecules. The results with an equivalent amount of water added indicate the incomplete formation of a hydrate $\text{CCl}_3\cdot\text{CO}_2\text{H}\cdot\text{H}_2\text{O}$.

