718. *The Kinetics of Catalytic Polymerisations. Part IX.* The State of the Chloroacetic Acids in Solution.*

By C. P. Brown and A. R. Mathieson.

The dimerisation and hydration of the chloroacetic acids in organic solvents is discussed. In inert solvents of low dielectric constant the acids exist very largely as dimers but high dielectric constant and ability of the solvent to form hydrogen bonds lead to considerable dissociation of the dimers. In a given solvent the more highly chlorinated acids are more highly associated. The association of acetic acid and the three chloroacetic acids has been studied in styrene and α-methylstyrene by a partition method, and cryoscopically in styrene in the presence and absence of water. The hydration of these acids in styrene and α-methylstyrene has been estimated. The presence of water causes dissociation of the dimers and reduces the strength of their hydrogen bonds. The cryoscopic constant of styrene is 4·32, and its freezing point −30·4°.

To formulate a mechanism for the chloroacetic acid-catalysed polymerisation of styrene we must identify the chemical species responsible for initiation, and so must know the nature of the acid species present and their concentrations.

The association of the chloroacetic acids in solution has already been studied in many solvents, and we have interpreted the data [1] relating to the partition of acetic acid and the chloroacetic acids between water and various organic solvents. The equilibria involved in these partitions can be represented as

$$H^+ + R{\cdot}CO_2^- \text{ (aq.)} \rightleftharpoons R{\cdot}CO_2H \text{ (aq.)}$$

$$R{\cdot}CO_2H \text{ (aq.)} \rightleftharpoons R{\cdot}CO_2H \text{ (org.)}$$

$$(R{\cdot}CO_2H)_2 \text{ (org.)} \rightleftharpoons 2R{\cdot}CO_2H \text{ (org.)}$$

and the first two equilibria may be written stoicheiometrically as

$$\text{Total acid (aq.)} \rightleftharpoons R{\cdot}CO_2H \text{ (org.)}$$

Two equilibrium constants define the system

$$K_1 = [R{\cdot}CO_2H \text{ (org.)}]/[\text{total acid (aq.)}] \text{ and } K_2 = [R{\cdot}CO_2H \text{ (org.)}]^2/[(R{\cdot}CO_2H)_2 \text{ (org.)}] \quad (1)$$

If c and f are the concentration and activity coefficient (moles $l.^{-1}$) in the aqueous phase, and c' the concentration in the organic phase,

then
$$c'/cf = K_1 + 2K_1^2cf/K_2 \quad (2)$$

By plotting cf against c'/cf, values of both K_1 and K_2 were obtained for the four acids in a number of solvents. All these results refer to water-saturated systems and both monomeric and dimeric species may be hydrated. The value of K_1 increases with the dielectric constant of the organic solvent. The value of K_2 is very low (*i.e.*, the acid exists very largely as dimer) in inert media of low dielectric constant, but high dielectric constant and ability of the solvent to form hydrogen bonds encourage the dissociation of the dimers. In a given solvent the more highly chlorinated acids are more highly associated.

Bell, Baughan, and Vaughan-Jackson [2] studied the association of the three chloroacetic acids in *p*-chlorotoluene cryoscopically and found that between 0·05 and 0·35 mole $l.^{-1}$ they are almost wholly present as dimers. The influence of water on the association of

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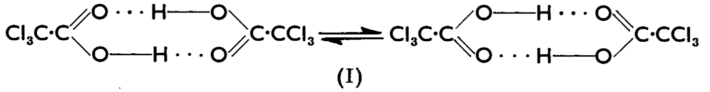
* Part VIII, preceding paper.

[1] Brown and Mathieson, *J. Phys. Chem.*, 1954, **58**, 1057.

[2] Bell, Baughan, and Vaughan-Jackson, *J.*, 1934, 1968.

trichloroacetic acid in benzene has been examined cryoscopically by Bell and Arnold,[3] who concluded that in dilute solutions most of the acid exists as the hydrated monomer $CCl_3{\cdot}CO_2H,H_2O$, but above 0·7 moles $l.^{-1}$ there is also present a significant amount of the dimeric dihydrate $(CCl_3{\cdot}CO_2H,H_2O)_2$. Clearly the dimeric dihydrate is less stable than the unhydrated dimer. Bell[4] (see also ref. 7) has suggested possible structures for these species. The unhydrated dimer may be represented as (I) and the hydrated monomer as (II) or (III)

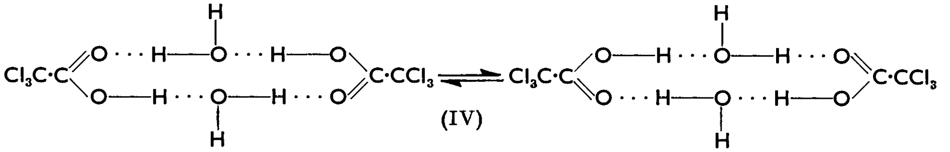


(I)

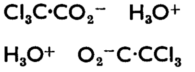
(II)

$Cl_3C{\cdot}CO_2^-,H_3O^+$ or $Cl_3C{\cdot}CO_2H_2^+OH^-$ (III)

Similarly the dimeric dihydrate may be (IV), (V), or (VI) : [5]

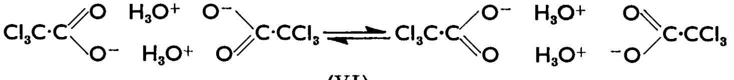


(IV)



$$\begin{matrix} Cl_3C{\cdot}CO_2^- & H_3O^+ \\ H_3O^+ & O_2^-C{\cdot}CCl_3 \end{matrix}$$

(V)



(VI)

It is not certain whether the hydrogen-bonded or the ionic form corresponds more closely with the actual structure. Davies, Jones, Patnaik, and Moelwyn-Hughes [6] believe that the bonding in the dimers is largely electrostatic, and this is supported by our conclusions [1] that high dielectric constant favours dissociation and that the more highly chlorinated acids are more highly associated, but the dissociation of the dimers in hydrogen-bonding solvents of low dielectric constant suggests that the hydrogen-bonded structures may contribute something to the state of the molecule.

The dimerisation and the hydration of the chloroacetic acids were studied in styrene and in α-methylstyrene by partition and cryoscopic methods and the hydration of the acids estimated.

RESULTS AND DISCUSSION

Partition of the Chloroacetic Acids between Styrene and α-Methylstyrene, and Water.—The partition results for the three chloroacetic acids and acetic acid distributed between styrene and water, and α-methylstyrene and water, at 25°, are summarised in Table 1. Fig. 1 shows a plot of c'/cf against cf for the four acids distributed between styrene and water, and illustrates the agreement of the results with eqn. (2), from which the values of K_1 and K_2 are calculated. The values of f were obtained from results quoted in ref. 1.

The values of both K_1 and K_2 increase from acetic to dichloroacetic acid but are lower for trichloroacetic acid. Evidently dichloroacetic acid is appreciably less dimerised than trichloroacetic acid, particularly in styrene.

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[3] Bell and Arnold, *J.*, 1935, 1432.

[4] Cf. Sidgwick, *Ann. Reports*, 1934, **31**, 40.

[5] Brown and Mathieson, *Ricerca Sci.*, 1955, **25**, Suppl. Simp. Int. Chim. Macromol.

[6] Davies, Jones, Patnaik, and Moelwyn-Hughes, *J.*, 1951, 1249.

TABLE 1. *Partition of the acids between water, and styrene and α-methylstyrene.*

	Styrene				α-Methylstyrene			
Acid	10^3K_1	10^3K_2	n	Dimer (moles %)	10^3K_1	10^3K_2	n	Dimer (moles %)
Acetic	2·0	0·44	1·7	82	3·6	2·0	1·6	75
Monochloroacetic	11	11	1·5	67	9·1	13	1·4	57
Dichloroacetic	59	89	1·4	57	22	14	1·4	57
Trichloroacetic	14	1·8	1·8	89	6·5	0·62	1·9	95

The partition can also be written stoicheiometrically as

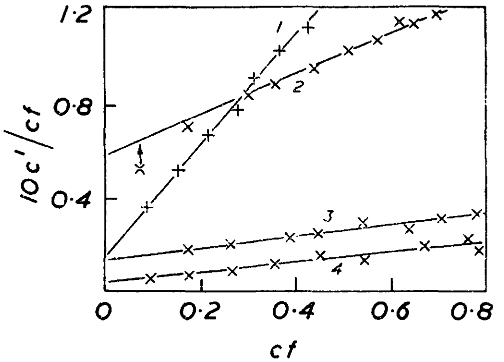
$$n\ \mathrm{R{\cdot}CO_2H\ (aq.)} \rightleftharpoons \mathrm{(R{\cdot}CO_2H)}_n\ \mathrm{(org.)}$$

where n is the stoicheiometric degree of association in the organic phase. Hence $c'/(cf)^n = K$

and
$$\log c' = \log K + n \log cf \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

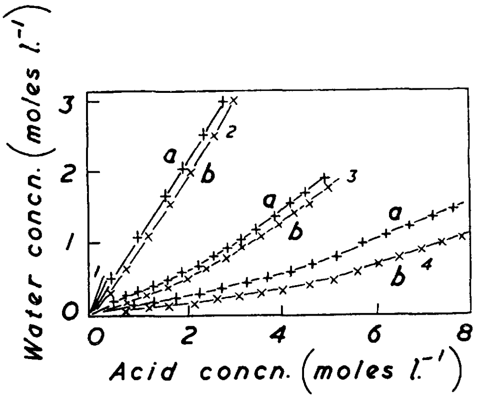
from which values of n can be obtained. Plots of log c' against log cf are linear over large ranges of concentration, indicating that n is insensitive to concentration when this is not too low. Table 1 includes the values of n so obtained and the corresponding percentage of the acid in the organic phase present in the dimeric form.

FIG. 1. *Partition of the chloroacetic acids between styrene and water at 25°.*



1, Trichloroacetic; 2, dichloroacetic; 3, monochloroacetic; 4, acetic acid.

FIG. 2. *Effect of the chloroacetic acids on the solubility of water in styrene and in α-methylstyrene at 25°.*



1, Trichloroacetic; 2, dichloroacetic; 3, monochloroacetic; 4, acetic acid; *a*, α-methylstyrene; *b*, styrene.

Hydration of the Acids in the Organic Phase.—Since in the partition experiments the organic phase is always water-saturated, and some water is necessary for polymerisation, the solubility of water in styrene and α-methylstyrene solutions of the acids was determined.

TABLE 2. *Hydration of the acids (mole ratios [water]/[acid]) at 25°.*

Solvent	$CH_3{\cdot}CO_2H$	$CH_2Cl{\cdot}CO_2H$	$CHCl_2{\cdot}CO_2H$	$CCl_3{\cdot}CO_2H$
Benzene	0·15	0·20	0·60	1·07
Styrene	0·25	0·51	1·25	1·30
α-Methylstyrene	0·20	0·54	1·30	1·11

The results are shown in Fig. 2. The variation of the water solubility with acid concentration approaches linearity at high acid concentrations, and Table 2 shows the mole ratios [water]/[acid] for this " linear " region, together with Bell's results[7] for benzene

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[7] Bell, *Z. phys. Chem.*, 1930, *A*, **150**, 20.

solution. The degree of hydration increases with the acid strength, exceeding unity for di- and tri-chloroacetic acid. It seems likely that this implies almost complete hydration of the acid species—monomeric and dimeric—in water-saturated solutions. However, no crystalline hydrate could be identified by measurements of the vapour pressure of a saturated solution of water in a styrene–trichloroacetic acid mixture from which the styrene was being progressively removed by evaporation in an apparatus similar to that described by Mathieson.[8]

Freezing-point Depression.—The association of the chloroacetic acids in styrene was studied cryoscopically in the presence of different concentrations of water. It was first necessary to determine the freezing point and cryoscopic constant of styrene. The calorimeter employed for the freezing-point measurements was that described by Brown, Mathieson, and Thynne,[9] and the equilibrium method was used. The freezing point of pure styrene was −30·4° ± 0·1°, which differs somewhat from that previously reported (−33°).[10]

Carbon tetrachloride was chosen as solute for the determination of the cryoscopic constant of styrene, since it seemed most likely to exhibit ideal behaviour. Even so, as some deviation from ideality is expected, plots of $\Delta T/m$ against m must be extrapolated to zero concentration (ΔT = freezing-point depression, m = molality of solute). The three sets of results differ slightly but all extrapolate linearly to the same value of $\Delta T/m$ at zero concentration, 4·32, and this is the cryoscopic constant of styrene.

The freezing points of solutions of acetic and the three chloroacetic acids in styrene were measured in the absence of water by Brown and Bury's method,[11] who used sodium sulphate as a drying agent within the solution. These results are given in Table 3, in which ΔT is the observed depression and ΔT_i that calculated for an ideal solution of monomeric acid molecules. The ratio $\Delta T_i/\Delta T$ gives the degree of association of the acid. Since the measurements had to be carried out at low temperatures careful exclusion of atmospheric moisture was essential. Results were also obtained for di- and tri-chloroacetic acid in the presence of water at saturation concentration, and these are shown in Table 4. The solubility of water in pure styrene is too low at −30·4° to depress the freezing point detectably.

The values of $\Delta T_i/\Delta T$ for water-saturated solutions can be compared with the values of n from the partition experiments, though it must be remembered that they refer to −30·4° and +25°, respectively. The values of $\Delta T_i/\Delta T$ are somewhat lower, and appear to decrease with increasing concentration; nevertheless both methods indicate a bigger

TABLE 3. *Association of the chloroacetic acids in styrene in the absence of water below* −30·4°.

m	ΔT	$\Delta T/m$	$\Delta T_i/m$	$\Delta T_i/\Delta T$	m	ΔT	$\Delta T/m$	$\Delta T_i/m$	$\Delta T_i/\Delta T$
		Acetic acid					Dichloroacetic acid		
0·25	0·62	2·48	4·24	1·71	0·22	0·46	2·09	4·24	2·03
0·40	1·01	2·51	4·18	1·67	0·37	0·77	2·09	4·26	2·01
0·64	1·53	2·39	4·13	1·73	0·60	1·24	2·07	4·14	2·00
0·93	2·26	2·43	4·04	1·66	0·81	1·67	2·06	4·08	1·98
1·26	3·03	2·40	3·94	1·64	1·07	2·11	1·97	4·00	2·03
		Monochloroacetic acid					Trichloroacetic acid		
0·21	0·49	2·32	4·24	1·83	0·097	0·20	2·11	4·29	2·03
0·39	0·85	2·19	4·19	1·91	0·15	0·32	2·13	4·28	2·01
0·68	1·49	2·19	4·13	1·89	0·27	0·58	2·15	4·23	1·97
0·97	2·12	2·18	4·03	1·85	0·38	0·81	2·12	4·20	1·98
1·38	3·04	2·20	3·98	1·81	0·49	1·04	2·12	4·17	1·97

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[8] Mathieson, *J.*, 1949, S 294.

[9] Brown, Mathieson, and Thynne, *J.*, 1955, 4141.

[10] Cf. Heilbron and Bunbury, "Dictionary of Organic Compounds," Eyre and Spottiswoode, London, 1943, Vol. 3, p. 643.

[11] Brown and Bury, *J. Phys. Chem.*, 1926, **38**, 694.

degree of association for trichloroacetic acid than for dichloroacetic acid, and when the different experimental conditions are considered, the values are in reasonable accord.

The values of $\Delta T_i/\Delta T$ in Tables 3 and 4 show clearly that the tendency to dimerise increases with the chlorine content of the acid, the dimerisation initially being complete for di- and tri-chloroacetic acid. The addition of water decreases the degree of dimerisation quite markedly.

TABLE 4. *Association of di- and tri-chloroacetic acid in styrene saturated with water below* 30·4°.

m	ΔT	$\Delta T/m$	$\Delta T_i/m$	$\Delta T_i/\Delta T$	m	ΔT	$\Delta T/m$	$\Delta T_i/m$	$\Delta T_i/\Delta T$
	Dichloroacetic acid					Trichloroacetic acid			
0·41	1·07	2·60	4·18	1·61	0·13	0·31	2·41	4·29	1·78
0·77	2·37	3·08	4·09	1·33	0·24	0·62	2·57	4·24	1·65
0·86	2·68	3·12	4·06	1·30	0·30	0·84	2·79	4·22	1·51
0·97	2·91	3·00	3·93	1·31	0·38	1·06	2·80	4·20	1·50

Effect of Water on the Extent of Dimerisation.—Di- and tri-chloroacetic acid are almost completely dimerised in water-free styrene solution. In solvents of higher dielectric constant and particularly those which can form hydrogen bonds, the degree of dimerisation is markedly reduced.[1] Water also facilitates the dissociation of the dimeric forms of the acids. Even in styrene, in the presence of water the concentration of the hydrated monomeric species (II or III) is considerable. In water-saturated solutions both monomer and dimer are fully hydrated, and presumably exist as (II) or (III) and (IV), (V), or (VI) respectively. Clearly the bonding is weaker in the dimeric dihydrate than in the unhydrated dimer, and this may be important in explaining both the rôle of water in the polymerisations and their high kinetic order with respect to the acid catalyst.

It is possible to obtain a more quantitative estimate of the effect of water on the dissociation of the dimers. In water-saturated and water-free solutions respectively, the association can be written as

$$2\mathrm{R{\cdot}CO_2H,H_2O} \rightleftharpoons \mathrm{(R{\cdot}CO_2H,H_2O)_2} \quad K_2 = [\mathrm{R{\cdot}CO_2H,H_2O}]^2/[(\mathrm{R{\cdot}CO_2H,H_2O})_2]$$

and

$$2\mathrm{R{\cdot}CO_2H} \rightleftharpoons \mathrm{(R{\cdot}CO_2H)_2} \quad K_3 = [\mathrm{R{\cdot}CO_2H}]^2/[(\mathrm{R{\cdot}CO_2H})_2]$$

If C_1 and C_2 are the concentrations of acid present as monomer and dimer respectively, then the degree of association

$$n = \Delta T_i/\Delta T = (C_1 + 2C_2)/(C_1 + C_2)$$

Also K_2 (or K_3) $= C_1^2/2C_2$.

Hence K_2 (or K_3) $= C_1\,(1 - n/2)/(n - 1)$ and values of K_2 and K_3 can be obtained at −30·4° from the freezing-point data for di- and tri-chloroacetic acid. Values of $\Delta G_2°$ and $\Delta G_3°$, the corresponding standard free-energy changes, can be calculated; they are 630 and 4460 cal. respectively for dichloroacetic acid and 1460 and 4590 cal. for trichloroacetic acid at −30·4°. The values for $\Delta G_3°$ (−30·4°) are only accurate to ±50%, since the values of n are close to 2·00; even so $\Delta G_3°$ clearly exceeds $\Delta G_2°$ by about 3 kcal. Thus water reduces the free energy of dissociation of the dimer by about 75%.

EXPERIMENTAL

Partition.—Aqueous solutions (20 ml.) of the chloroacetic acids of various concentrations were added to styrene (20 ml.) or α-methylstyrene (20 ml.) in 50-ml. vessels, and equilibrated for 2—3 hr. at 25° ± 0·01° with continuous agitation. The layers were separated and titrated with 0·1 or 0·01N-alkali solutions.

Water Solubilities.—Water was added from a microburette to solutions of the chloroacetic acids in styrene or α-methylstyrene until turbidity appeared.

Freezing Point and Cryoscopic Constant of Styrene.—The calorimeter described by Brown, Mathieson, and Thynne [9] was used, except that the mixing vessel was replaced by a glass vessel which fitted closely into the innermost Dewar vessel, and carried a stirrer, platinum resistance thermometer, dropping pipette, and sampling tube. Styrene, purified and dried, was distilled into this glass vessel which was then closed and placed in a solid carbon dioxide–alcohol freezing bath. A film of solid styrene formed on the inner surface of the vessel and was shaken free from time to time. In this way, 250 ml. of a sludge of liquid and solid styrene were prepared, containing about 50% of solid. The glass vessel was introduced into the inner Dewar vessel which was surrounded by the cryostatic liquid (solid carbon dioxide–alcohol), kept about 1° below the temperature of the inner Dewar vessel by addition of solid carbon dioxide and the use of a 20-junction thermocouple. The inner Dewar vessel carried a metal lid which also dipped into this cryostatic liquid. The calorimeter was assembled, stirring commenced at 60 revs. per min., and the apparatus left for 2 hr. to attain equilibrium. The temperature of the styrene sludge was measured by the platinum resistance thermometer.

Concentrated solutions of carbon tetrachloride in styrene, previously cooled to the equilibrium temperature, were placed in the dropping pipette and added to the styrene sludge without opening the calorimeter by raising a projecting glass rod which controlled the dropping pipette. 20 min. were allowed for equilibrium to be attained after the addition of carbon tetrachloride solution, the temperature was read and stirring discontinued. The sampling tube, previously evacuated to 10—20 mm. pressure, was opened to the solution and a suitable quantity withdrawn for analysis.

The carbon tetrachloride solutions in styrene were analysed densitometrically. The pycnometer was a 5-ml. glass bulb carrying a capillary tube, and this was calibrated at 25° with water and a cathetometer.

Freezing points of solutions of chloroacetic acid in styrene were determined in the same way as the carbon tetrachloride solutions, but the solutions were analysed by alkali titration. For the experiments in the absence of water the glass vessel contained 10 g. of anhydrous sodium sulphate (" AnalaR "). Otherwise, the required amount of water was added with the chloroacetic acid.

No polymerisation occurred in any of these experiments.

Materials.—Carbon tetrachloride was washed with alcoholic potassium hydroxide and with water, dried ($CaCl_2$), and fractionated. The chloroacetic acids, styrene, and α-methylstyrene were purified as described previously.[12]

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[12] Brown and Mathieson, Part VI, *J.*, 1957, 3608.