281. *Chemical Constitution and the Dissociation Constants of Monocarboxylic Acids. Part XVIII.* Some Acetic and Propionic Acids Substituted with Hydrocarbon Radicals in* 10% *and* 25% *(w/w) Acetone–Water Solutions.*

By J. F. J. DIPPY, S. R. C. HUGHES, and A. ROZANSKI.

The thermodynamic dissociation constants of a series of acetic and propionic acids progressively substituted with alkyl and phenyl groups have been measured conductimetrically in 10% and 25% (w/w) acetone–water solutions at 25°. Steric effects on ionisation were studied by plotting (i) log K against the reciprocal of the dielectric constant of the solvent (including data for aqueous solutions), and (ii) log K in the first solvent against log K in the second. Acetic acids substituted with two or more bulky groups are weakened by lowering the solvent dielectric constant appreciably more than are similar β-substituted propionic acids and monosubstituted acetic acids; this is attributed to steric inhibition of solvation. Unexpectedly, acetic acid, and probably propionic acid also, show behaviour different from that of other acids free from steric effects, and this cannot be simply explained.

THERE are few results for the dissociation constants of carboxylic acids in non-aqueous and partially aqueous solvents, although they have been accumulating.[1] The relative change of strength of an acid in different solvents is governed by the basicity and dielectric constant of the solvent, and by any specific solvent–solute interactions which affect ionisation. It is generally held [2] that the sequence of strengths of acids in which the substituents do not exert appreciable spatial effects on the proton transfer site is the same in different solvents; where, however, such effects exist different sequences may be observed in different solvents (*e.g.*, *ortho*-substituted benzoic acids). Furthermore, provided that the solvents are constitutionally similar it is possible to apply the well-known correlation log $K \propto 1/D$ (D = dielectric constant) [3] (generally for $D > 25$). It follows that for acids free from any steric effect the slopes of the lines in the log K *versus* $1/D$ plot are almost identical, and that a plot of log K' (in one solvent) against log K'' (in a second solvent) should be a straight line with unit slope; for sterically-hindered acids, plots of log K against $1/D$ have varying slopes, and the points do not fall on a straight line in the log K' *versus* log K'' plot.[5,6] The present investigation was carried out to supply

---

* Part XVII, *J.*, 1957, 2405.

[1] Izmailov, *Zhur. fiz. Khim.*, 1950, **24**, 321.

[2] Ingold, "Structure and Mechanism in Organic Chemistry," Bell & Sons, London, 1953.

[3] Wynne-Jones, *Proc. Roy. Soc.*, 1933, *A*, **140**, 440.

[4] Kilpatrick, *Chem. Rev.*, 1933, **13**, 136.

[5] Dippy and Davey, *J.*, 1944, 411.

[6] Wooten and Hammett, *J. Amer. Chem. Soc.*, 1935, **57**, 2289.

more evidence for the above feature, and to determine whether a study of acid strengths in chemically similar solvents could distinguish between acids whose electrolytic dissociation is determined solely by polar effects, and those in which steric effects play a substantial, additional rôle.

The mean values of the thermodynamic dissociation constants in aqueous acetone solutions determined by the authors, and those from the literature for aqueous solutions, are shown in Table 1.

Aqueous acetone was chosen as a compromise between the solubility requirements of some of these acids and the theoretical and practical difficulties accompanying measurements in pure non-aqueous solvents. The basicities of these solvents (as measured by the acidity function, H_0, interpolated from the Braude's results 7) are given in Table 2; this trend, combined with the decrease in dielectric constant of the solvent as the percentage of acetone increases, progressively lowers the acid strengths.

TABLE 1. *Mean values of thermodynamic dissociation constants* (10^5K *at* 25°) *and melting or boiling points.*

Acid	10% Acetone–water	25% Acetone–water	Water *	$-\Delta \log K/\Delta 1/D$ (mean)	M. p.	M. p. (lit.) ‡
Acetic	1·25	0·585	1·75[a]	160·0	118° †	118·1°
Propionic	1·03	0·363	1·34[b]	176·0	141 †	141·1
Trimethylacetic	0·586	0·162	0·891[a]	238·0	274	265
β-Phenylpropionic	1·26	0·403	2·19[c]	251·0	50	49·5
Phenylacetic	2·71	0·861	4·88[d]	259·0	76·5	76
Benzoic	3·52	1·01	6·27,[e] 6·53[f]	279·0	122·2	122
ββ-Dimethyl-β-phenylpropionic	0·536	0·154	—	281·0	60	58·5
ββ-Diphenylpropionic	1·48	0·420	—	284·0	155·2	155
Methylneopentyl-t-butylacetic (Siccatic B)	0·0680	0·0151	—	339·0	132—132·5	130
Diphenylacetic	4·76	0·958	11·5[d]	376·0	148·5	148
Triphenylacetic	4·26	0·802	—	376·0	274	265
Dineopentylacetic (Siccatic A)	0·384	0·0667	—	394·0	86·5—87	55

* Best conductimetric values from literature. † B. p. at 769 mm. Trimethylacetic acid had b. p. 118°/769 mm. (lit. 118·1°). ‡ Best value from literature.

[a] Dippy, *J.*, 1938, 1222. [d] Dippy and Williams, *J.*, 1934, 161. [b] Belcher, *J. Amer. Chem. Soc.*, 1938, **60**, 2744. [c] Dippy and Lewis, *J.*, 1937, 1008. [e] Dippy and Williams, *J.*, 1934, 1888. [f] Ives, *J.*, 1933, 561.

TABLE 2. *Acidity functions,* H_0, *for aqueous acetone solutions* (*from Braude* 7).

		H_0	
	Water	10% Acetone–water	25% Acetone–water
0·1M-HCl	1·01	1·14	1·41
1M-HCl	−0·33	−0·12	0·28

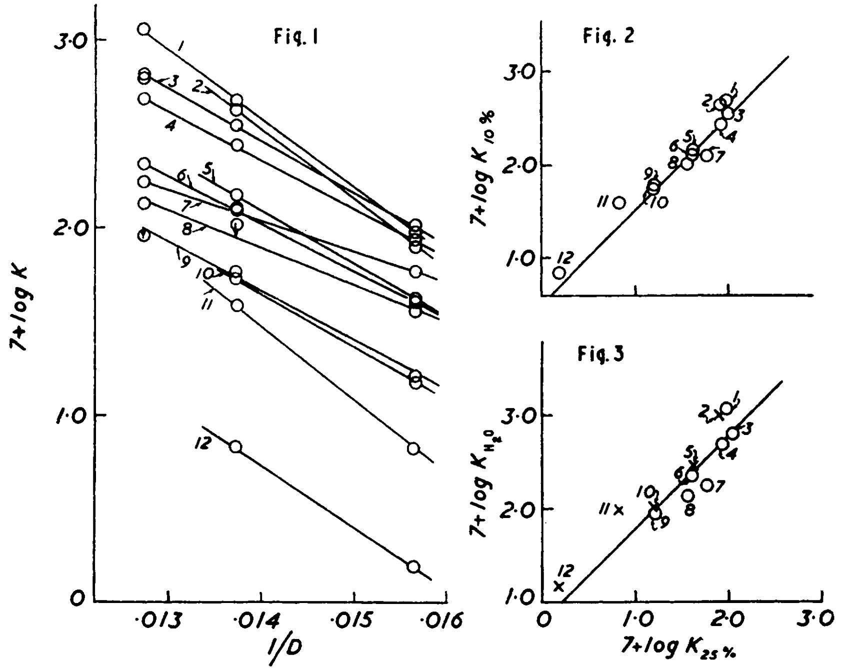
The plot of log K against $1/D$ (Fig. 1) shows that, where the values of K in the three media are available, good straight lines are obtained (trimethylacetic and propionic acids showing the poorest correlations). The acids fall into three groups as regards the relative magnitudes of the slopes: (i) monosubstituted acetic acids, trimethylacetic acid, and mono-, di-, and tri-β-substituted propionic acids (and benzoic acid as reference), (ii) di- and tri-substituted acetic acids (except trimethylacetic), and (iii) acetic acid. In the plot of log K' against log K'' the first group lies approximately on a straight line of unit slope, whilst the points representing the acids of the second group are above this line and those for acetic acid (and propionic acid in water) fall below it (Figs. 2 and 3). This classification shows that considerations of the size of the substituent and its distance from the carboxyl group govern qualitatively the behaviour of these acids in the solvents. Both small and large substituents in the β-position influence the relative change of strengths in aqueous acetone in the same degree as a single substituent in acetic acid. On the other hand, two

---

[7] Braude, *J.*, 1948, 1976.

or three bulky substituents (phenyl, neopentyl, and t-butyl, but not methyl) on the α-carbon atom sharply decrease the relative strength in aqueous acetone (exhibited by steeper slopes in Fig. 1), *e.g.*, triphenylacetic and siccatic acids show unusually large depression of strength in these solvents (cf. ref. 8). The primary steric effect must be considered to operate here. The energy of solution of the carboxylate ion is greater than that of the undissociated acid molecule, so steric compression of the carboxyl group in hindered acids preferentially inhibits solvation of the anion, thus diminishing the ionic concentration in the dissociation equilibrium, *i.e.*, acid strength falls. This effect becomes more marked as the percentage of acetone in the solvent increases, *i.e.*, as anion solvation becomes increasingly difficult.

FIGS. 1—3. For key to numbers see Table 4.



FIG, 3, × Values for water obtained from log K–$1/D$ relationship.

With acetic acid and, probably, propionic acid, factors apparently operate which produce an effect opposite to that created when bulky substituents compress the carboxyl group (Figs. 2 and 3). It is possible that, owing to the relatively small size of these molecules, some specific interactions, easily influenced by the nature of the solvent, occur, but it is difficult to speculate as to their nature.

This work emphasises the view that a comparison of monocarboxylic acid strengths in two or more related solvents furnishes a criterion of the operation of steric factors in the dissociation of carboxylic acids, and this method of comparison may be applicable to other acid systems to differentiate between the diverse steric factors.

EXPERIMENTAL

Preparation and Purification of Acids.—Triphenylacetic acid (from Dr. Weedon of Imperial College, London) and siccatic acids A and B (from Alchemy Ltd.) were gifts which we gratefully acknowledge. ββ-Diphenylpropionic and ββ-dimethyl-β-phenylpropionic acids were prepared

---

[8] Hammond and Hoyle, *J. Amer. Chem. Soc.*, 1955, **77**, 338; Kilpatrick and Fachenthal, *J. Electrochem. Soc.*, 1953, **100**, 185.

TABLE 3. *Physical constants of the solvents.*

	d_4^{25}	η_0^{25}	D_{25} * (H_2O = 78·6)
10% (w/w) Acetone–water	0·9832	0·01105	73·0
25% (w/w) Acetone–water	0·9618	0·01335	64·0

* From Harned and Owen, " Physical Chemistry of Electrolyte Solutions," Reinhold, New York, 1950, p. 118.

TABLE 4. *Conductivities.*

10^3C (equiv./ l.)	Λ (mho cm.²)	10^5K	10^3C (equiv. l.)	Λ (mho cm.²)	10^5K	10^3C (equiv./ l.)	Λ (mho cm.²)	10^5K	10^3C (equiv./ l.)	Λ (mho cm.²)	10^5K
(10% Acetone–water)						(25% Acetone–water)					
Acetic acid (7)											
2·231	20·76	1·26	1·054	29·53	1·25	1·916	10·03	0·585	0·5906	17·56	0·581
1·731	23·37	1·25	0·6332	37·64	1·26	1·707	10·62	0·586	0·4240	20·68	0·586
1·489	25·20	1·26	0·2171	59·86	(1·21)	1·430	11·55	0·585	0·3111	23·78	0·584
1·308	26·67	1·25				0·8842	14·49	0·581	0·2336	27·18	0·590
	(Λ_0 = 284·3)						(Λ_0 = 184·7)				
Phenylacetic acid (4)											
2·177	31·04	2·71	1·143	41·86	2·71	2·066	12·43	0·862	0·8289	19·21	0·862
1·684	35·03	2·71	0·6520	52·79	(2·58)	1·768	13·38	0·859	0·7562	20·05	0·862
1·460	37·40	2·71	0·3583	70·43	2·73	1·230	15·88	0·857	0·4633	25·19	0·860
						0·9891	17·67	0·862	0·1806	38·67	0·861
	(Λ_0 = 290·8)						(Λ_0 = 196·5)				
Diphenylacetic acid (1)											
1·264	52·18	4·76	0·5126	77·23	4·76	1·883	14·17	0·958	0·3883	29·79	0·960
1·160	54·18	4·76	0·4187	84·01	4·75	1·732	14·73	0·955	0·3126	32·90	0·961
1·062	56·34	4·75	0·3222	93·60	4·76	1·609	15·29	0·960	0·2028	39·85	0·955
0·7478	65·77	4·76	0·1983	113·1	4·76	0·9195	19·90	0·956			
0·6106	71·79	4·77					(Λ_0 = 203·5)				
	(Λ_0 = 292·8)										
Triphenylacetic acid (2)											
0·05012	(135·6)	—	0·03311	194·4	4·15	0·1991	35·67	0·801	0·1110	46·08	0·799
0·03981	187·7	4·47	0·03121	194·9	4·05	0·1377	42·05	0·803	0·09700	48·86	0·800
	(Assumed Λ_0 = 294·0)					0·1228	44·26	0·806	0·07169	55·53	0·801
							(Assumed Λ_0 = 195·5)				
Trimethylacetic acid (9)											
1·732	14·66	0·589	0·3845	29·94	0·586	1·952	5·336	0·164	0·4474	10·88	0·162
1·230	17·27	0·588	0·2431	36·94	0·583	1·602	5·783	0·159	0·2516	14·29	0·161
0·9215	19·83	0·588	0·2140	39·17	0·583	1·233	6·680	0·164	0·1751	16·02	(0·142)
0·4827	26·95	0·588					(Λ_0 = 185·3)				
	(Λ_0 = 256·7)										
Dineopentylacetic acid (*siccatic acid A*) (11)											
0·1658	40·41	0·385	0·09655	51·15	(0·376)	0·6462	6·377	0·0672	0·4635	7·544	0·0679
0·1233	46·31	0·386	0·08201	55·31	0·381	0·6303	6·423	0·0665	0·3252	8·879	0·0665
0·1185	47·07	0·384	0·07715	56·91	0·382	0·4942	7·201	0·0659	0·2038	11·07	0·0656
	(Assumed Λ_0 = 285·0)					0·4701	7·501	0·0681	0·1291	13·83	0·0659
							(Assumed Λ_0 = 200·0)				
Methylneopentyl-t-butylacetic acid (*siccatic acid B*) (12)											
0·07782	24·84	0·0669	0·06564	27·30	0·0689	0·3262	3·883	0·0146	0·1882	5·227	0·0154
0·06665	26·93	0·0680	0·05749	28·90	0·0680	0·2762	4·288	0·0151	0·07425	9·087	(0·0188)
	(Assumed Λ_0 = 280·0)					0·2277	4·713	0·0151			
							(Assumed Λ_0 = 185·0)				
Propionic acid (8)											
1·972	18·36	1·028	1·030	25·00	1·028	2·106	7·499	0·364	1·041	10·55	0·364
1·633	20·08	1·028	0·7587	28·83	1·025	1·717	8·293	0·365	0·6656	13·00	0·358
1·497	20·95	1·028	0·4390	37·24	1·029	1·675	8·345	0·360	0·4015	16·66	0·364
1·204	23·23	1·029	0·2890	45·04	1·028	1·484	8·880	0·363			
	(Λ_0 = 261·0)						(Λ_0 = 182·5)				

TABLE 4. (*Continued.*)

10^3C (equiv./l.)	Λ (mho cm.^{2})	10^5K	10^3C (equiv./l.)	Λ (mho cm.^{2})	10^5K	10^3C (equiv./l.)	Λ (mho cm.^{2})	10^5K	10^3C (equiv./l.)	Λ (mho cm.^{2})	10^5K
(10% Acetone–water)						(25% Acetone–water)					
β-Phenylpropionic acid (6)											
2·039	21·76	1·26	0·6273	37·92	1·26	1·863	8·964	0·402	1·032	11·95	0·403
1·789	23·16	1·26	0·3610	48·78	1·26	1·786	9·168	0·403	0·8079	13·44	0·403
1·153	28·54	1·26	0·1965	63·73	1·25	1·544	9·818	0·402	0·4329	18·10	0·402
0·7839	34·20	1·26				1·428	10·21	0·403	0·1894	26·67	0·403
	(Λ_0 = 285·4)						(Λ_0 = 195·7)				
ββ-Diphenylpropionic acid (5)											
1·299	29·27	1·48	0·6196	41·32	1·48	1·656	9·138	0·419	0·4287	17·48	0·420
1·191	30·53	1·48	0·4468	48·11	1·49	1·567	9·395	0·420	0·2960	20·84	0·420
0·8144	36·52	1·49	0·3157	56·02	1·48	1·173	10·80	0·420	0·2173	24·06	0·420
0·7151	38·82	1·49	0·1985	68·39	1·47	0·5053	16·17	0·420	0·1934	25·38	0·420
	(Λ_0 = 286·8)						(Λ_0 = 184·6)				
ββ-Dimethyl-β-phenylpropionic acid (10)											
1·842	14·92	0·537	0·4863	28·19	0·536	1·964	5·295	0·155	0·3897	11·64	0·154
1·502	16·45	0·536	0·4182	30·31	0·537	1·263	6·583	0·155	0·3068	13·06	0·154
1·254	17·99	0·539	0·3146	34·59	0·536	0·6536	9·057	0·154	0·2148	15·50	0·154
0·6538	24·52	0·537	0·2257	40·21	0·532	0·4929	10·38	0·154			
	(Λ_0 = 281·5)						(Λ_0 = 190·0)				
Benzoic acid (3)											
2·274	34·48	3·52	0·4990	68·23	3·52	2·292	13·28	1·01	0·6575	24·00	1·01
2·006	36·39	3·49	0·4232	73·37	3·54	1·975	14·27	1·01	0·4014	30·20	1·01
1·229	45·64	3·50	0·3366	80·80	3·54	1·630	15·64	1·01	0·2230	39·36	1·01
0·6750	59·75	3·51	0·2028	99·26	3·54	1·243	17·80	1·01	0·1820	42·98	1·01
	(Λ_0 = 291·0)						(Λ_0 = 204·3)				

by Dr. J. T. Young.[9] Other acids were purchased. Solid acids (with two exceptions) were repeatedly recrystallised from conductivity water (di- and tri-substituted acetic and propionic acids, being sparingly soluble, required up to 1 l. for 1 g. of acid). Siccatic acids A and B were recrystallised three times from small amounts of purified acetone, as water proved ineffective. "AnalaR" acetic acid was distilled twice from 2% (w/w) potassium permanganate (about 50% being rejected) and then fractionated. Propionic acid ("purified" quality) was fractionated twice. Trimethylacetic acid was distilled under reduced pressure in an all-glass apparatus.

The final specimens were stored in desiccators over silica gel for at least two weeks, and the m. p.s (Table 1) determined. Equivalent weights of all purified acids were derived by titration with alkali.

Purification of Acetone.—"AnalaR" acetone was fractionated in an all-glass distillation apparatus with a 14 in. column packed with Fenske helices, the heating being by a finely controlled Electrothermal mantle. The middle fraction (about 70%), boiling over a range of not more than 0·2°, was collected. Water contents of the resulting solvent and a few wetted samples (up to 5% of water by weight) were determined by the Karl Fischer technique,[10] and the correlation between water contents and physical properties was in agreement with the relationships given by S. R. C. Hughes: [11] $d_4^{25} = 0\cdot7835 + 0\cdot0031x$; $\eta_0^{25} = 0\cdot00300 + 0\cdot00017x$ (where x = % wt. of water). The density of each batch of acetone used for conductivity measurements was determined (100 ml. pyknometer), and the percentage of water calculated by use of the above equations. The mixed solvent (composition accurate to within ±0·01%) was prepared by weight in capped 2 l. conical flasks and allowed to stand for a few hours before use (for very sparingly-soluble acids it was much quicker to dissolve the solid in acetone and then make up by weight with water). The specific conductivities of the 10% and 25% aqueous acetone solutions were 0·5—0·6 gemmho and 0·2—0·3 gemmho respectively, at 25°.

[9] See Dippy and Young, *J.*, 1952, 1817; 1955, 3919.

[10] Mitchell and Smith, "Aquametry," Interscience, New York, 1948.

[11] S. R. C. Hughes, *J.*, 1956, 998.

Measurement of Conductivities and Calculation of Results.—Conductivities of all solutions were measured as previously described.[12]

Solvent corrections in non-aqueous and partially aqueous solvents are still problematical, since the nature of the impurities must be first established. No solvent correction was applied to aqueous solutions in this work, on the assumption that carbonic acid is the main impurity and its ionisation would be suppressed correspondingly by the addition of organic solvent to water.[13] This was justified by the consistent values of K obtained with " uncorrected " conductivity data.

Λ_0 was evaluated by Ives's extrapolation method [14] by use of appropriate physical constants for the solvents, as shown in Table 3; individual values of K were then calculated as usual. For triphenylacetic acid and siccatic acids (A and B), Λ_0 values were assumed, since the low solubility of these acids did not permit the use of extrapolation. The success of the extrapolation as applied to partially aqueous solvents is shown by (i) the constancy in the values of K over the range where the limiting Debye–Hückel law applies, (ii) the satisfactory correlation of K values in different solvents, as shown in Fig. 1, and (iii) the fluctuations in Λ_0 for different acids in each solvent which show the expected change of about ± 10 units about a mean value (although the plot of $\Lambda_0\eta$ against η reveals a regular decrease indicating, presumably, change in the mode of solvation of the ions).

One of us (A. R.) thanks the Governing Body of the Chelsea College of Science and Technology for a Research Assistantship.

CHEMISTRY DEPARTMENT, CHELSEA COLLEGE OF SCIENCE AND TECHNOLOGY,
LONDON, S.W.3. [*Received, September 26th*, 1958.]

---

[12] Dippy, S. R. C. Hughes, and Laxton, *J.*, 1954, 1470.
[13] Speakman, *Trans. Faraday Soc.*, 1954, **50**, 236.
[14] Ives, *J.*, 1933, 731; 1943, 511.