CXCI.—*The Dissociation Constants of Organic Acids. Part I. The Primary Dissociation Constants of Some Alkyl Malonic Acids.*

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In the series of researches of which the present paper forms the first part, it is proposed to investigate the relation between dissociation and allied constants and chemical constitution; especial attention will be given to such problems as (*a*) the influence of substituents and of unsaturation and (*b*) the effect of ring closure. The present communication is concerned with the investigation of malonic acid and seven alkyl-substituted malonic acids.

No accurate conductivity measurements of dibasic acids have hitherto been made. The early measurements of Ostwald (*Z. physikal. Chem.*, 1889, **3**, 282), of Bethmann (*ibid.*, 1890, **5**, 403), of Walden (*ibid.*, 1891, **8**, 449), and of Smith (*ibid.*, 1898, **25**, 200) can only be regarded as approximate owing to (1) the use of poor conductivity water and (2) the difficulties of manipulation attendant on the Ostwald–Arrhenius method of dilution. The values of μ_0, the conductivity at infinite dilution of the dibasic acid ionising as a uni-univalent electrolyte, employed by all previous workers were largely empirical and hence the resultant primary dissociation constants were likewise empirical. The recent work of Ferguson and Vogel (*Phil. Mag.*, 1925, **50**, 971; 1927, **4**, 1, 233, 300; *Trans. Faraday Soc.*, 1927, **23**, 404; compare *Ann. Reports*, 1927, **24**, 24; Vogel, *Phil. Mag.*, 1928, **5**, 199), more especially the development of a method for the calculation of the conductivity at infinite dilution free from all theoretical objections and the evaluation of the mobilities (or ionic conductivities) of the hydrogen, sodium, and potassium ions at 25°, has provided the necessary means whereby more probable values of μ_0 and hence of the primary dissociation constant of each individual dibasic acid may be computed.

In the accurate measurement of the conductivities of acids extending to dilutions of the order of 10^{-4} molar, the fundamental difficulty is that due to the solvent (compare Kendall, *J. Amer. Chem. Soc.*, 1916, **38**, 2460; 1917, **39**, 9; Washburn, *ibid.*, 1918, **40**, 106). By the use of the conductivity cell designed by Hartley and Barrett (J., 1913, **103**, 789), no difficulty was experienced, when working with equilibrium water of specific conductivity $0{\cdot}8$—$0{\cdot}9 \times 10^{-6}$ mho, in maintaining the conductivity of the solvent constant during an experiment; in this way the proportion of the total conductivity due to the solvent was accurately known. Further, owing to the relatively large solubilities of most of the compounds employed, it was found practicable to adopt the method suggested by Whetham (*Phil. Trans.*, 1900, **194**, 321; compare Frazer and Hartley, *Proc. Roy. Soc.*, 1925, *A*, **109**, 351) whereby to a known volume of pure solvent are added successive portions of a solution of a solute from a weight pipette, up to a concentration of the order of 10^{-2} molar.

EXPERIMENTAL.

Water. The water employed was prepared by the distillation of ordinary distilled water, to which some potassium permanganate and sodium hydroxide had been added, in a modified Bourdillon still (J., 1913, **103**, 791; compare Kraus and Dexter, *J. Amer. Chem. Soc.*, 1922, **44**, 2469) in which the carbon dioxide and other impurities were removed by fractional condensation. The distillation was conducted in a slow stream of air, purified by passage through three long tubes filled with soda–lime (" Sofnolite "), and when the water attained a specific conductivity of $0{\cdot}8$—$0{\cdot}9 \times 10^{-6}$ mho it was collected separately in special flasks. These were constructed wholly of Pyrex glass and each consisted of a 3-litre flask, the mouth of which was connected by means of a good ground-glass joint with a " head " carrying a siphon tube which had a tap at its lower end and was connected at its upper end through a tap and a ground-glass joint to a soda–lime guard tube. The joints were lubricated with pure vaselin. The conductivity-water containers were thoroughly cleaned with chromic acid mixture, steamed out with steam generated from distilled water for at least 12 hours, and then " seasoned " by standing full of conductivity water for one year, the water being replaced fortnightly. Equilibrium water could be kept in these containers for at least two months without appreciable change. The water used in all the final experiments had a specific conductivity of $0{\cdot}8$—$0{\cdot}9 \times 10^{-6}$ mho.

Acids. Malonic, methylmalonic, ethylmalonic, and diethylmalonic acids were prepared and purified for this research by Messrs. Boot and required no further purification. Dimethyl-, methylethyl-, and di-*n*-propyl-malonic acids were Kahlbaum's purest products and were recrystallised from organic solvents before use. The preparation of ethyl-*n*-propylmalonic acid is given below.

Malonic acid. Boot's malonic acid was recrystallised from benzene–ether containing 5% of light petroleum (b. p. 60—80°). M. p. 136° (decomp.); M = 104·03.

Methylmalonic acid. M. p. 132° (decomp.); M = 118·05.

Ethylmalonic acid. M. p. 115° (decomp.); M = 132·06.

Dimethylmalonic acid. Recrystallised from benzene–ether–light petroleum (b. p. 60—80°). M. p. 193·5° (decomp.); M = 132·06.

Methylethylmalonic acid. Recrystallised from benzene–ether–light petroleum (b. p. 60—80°). M. p. 121°; M = 146·08.

Diethylmalonic acid. M. p. 127°; M = 160·10.

Ethyl-n-*propylmalonic Acid.*—Pure ethyl malonate was converted by sodium ethoxide and ethyl iodide into ethyl ethylmalonate, b. p. 208—210°/765 mm., and the latter by sodium ethoxide and *n*-propyl iodide into ethyl ethyl-*n*-propylmalonate, b. p. 236°/763 mm. The last-named ester was hydrolysed with alcoholic potassium hydroxide, and the resultant acid recrystallised twice from benzene–ether–light petroleum (b. p. 40—60°) and finally from chloroform–light petroleum (b. p. 60—80°). It then melted at 116°; M = 174·11.

Di-n-*propylmalonic acid.* Recrystallised from chloroform. M. p. 161° (decomp.); M = 188·13.

The acids were dried in a vacuum desiccator over calcium chloride and paraffin wax for several days before use.

Disodium salts. The disodium salts of malonic, methylmalonic, ethylmalonic, and diethylmalonic acids were prepared and purified by Messrs. Boot. All the other disodium salts were prepared by adding the calculated quantity of N-sodium hydroxide solution, prepared from A.R. sodium hydroxide and standardised against A.R. potassium hydrogen phthalate, to the pure acid, evaporating the solution to dryness on the steam-bath, and recrystallising the product from dilute methyl or ethyl alcohol. Disodium methyl-, dimethyl-, ethyl-*n*-propyl- and di-*n*-propyl-malonates were recrystallised from dilute ethyl alcohol, and disodium methylethylmalonate from dilute methyl alcohol. All the salts were dried at 120—130° for at least 6 hours and then kept in a vacuum desiccator over calcium chloride or phosphoric oxide until required. The molecular weights employed were as follows: malonate 148·02 (compare Lorenz and Scheuermann, *Z. anorg. Chem.*, 1921, **117**, 121), methyl- 162·03, ethyl- 176·05, dimethyl- 176·05, methylethyl- 190·06, diethyl- 204·08, ethyl-*n*-propyl 218·10, and di-*n*-propyl- 232·11.

Measurement of resistance. The bridge assembly was of the normal Wheatstone type, the source of current being connected to the sliding contact and the junction of the standard resistance to the cell. The sliding contact was earthed. A Leeds and Northrup drum-wound, slide-wire bridge with extension coils and having an ebonite hood was employed. The slide wire was about 5 metres long and of 7 ohms resistance; it was calibrated by the method of Strouhal and Barus and found to have no appreciable error. The standard resistance box was a Cambridge and Paul low-induction resistance box of the dial type: it had a maximum resistance of 11,110 ohms and was accurate to 0·04%. A Brown telephone with adjustable diaphragm and of 150 ohms resistance was employed. Two condensers were used to balance out the effects of induction and capacity in the circuit; they were placed in parallel with the resistance and consisted of (i) a Sterling variable air condenser of maximum capacity 0·001 microfarad, for fine adjustment, and (ii) a step-up mica-condenser of maximum capacity 1·0 microfarad and minimum capacity 0·001 microfarad. Both condensers were always necessary except for the very dilute solutions. The bridge, resistance box, and condensers were mounted on slabs of paraffin wax.

The source of alternating current was a valve-oscillator constructed by Dr. A. R. Martin of this College, and gave a pure sine-wave alternating current of frequency 1000 cycles per second. It was placed in an adjoining room and was connected to the bridge by a lead-covered cable.

The conductivity cells. The three glass cells employed in the research were of Pyrex glass: two were constructed as described by Hartley and Barrett (*loc. cit.*); the first had a capacity of 550 c.c. with stout platinum electrodes 2·3 cm. × 3·3 cm. and 2·5 mm. apart, the second had a capacity of 350 c.c. with platinum electrodes 2·5 cm. × 1·8 cm. and 2·5 mm. apart. The electrodes were coated with grey platinum by Messrs. Johnson and Matthey. The third cell was a stoppered, round-bottomed glass bottle of about 20 c.c. capacity; the electrodes consisted of two grey-platinised platinum discs 1 cm. in diameter and about 5 mm. apart, which were sealed through the sides. The last cell was employed only for the measurement of the specific conductivity of the solvent, since this was outside the range of the other cells (compare Washburn, *J. Amer. Chem. Soc.*, 1916, **38**, 2431).

Temperature control. The thermostat was filled with distilled water and was electrically controlled with a mercury–toluene thermo-regulator; the temperature was constant at 25° ± 0·01°. The temperature was measured on a standard thermometer which had been recently calibrated at the National Physical Laboratory.

Balances. Two balances were used, a large Oertling balance, with a maximum load of 1500 g. and sensitive to 0·5 mg., for weighing the conductivity cells and the flask for the determination of cell constants, and a Bunge balance, specially overhauled for this research by Messrs. Oertling, of maximum load 75 g. and sensitive to 0·02 mg. The weights used were calibrated directly against a standard set which had recently been adjusted at the National Physical Laboratory.

Determination of cell constants. The constants of the three cells were determined directly with 0·01*N*-potassium chloride solution prepared with water having a specific conductivity of $0·9 \times 10^{-6}$ mho according to Parker and Parker (*J. Amer. Chem. Soc.*, 1924, **46**, 312). A litre resistance-glass flask and two small Pyrex weighing-bottles were used and were thoroughly cleaned and steamed out before use. The potassium chloride (Kahlbaum's purest) was recrystallised twice from conductivity water, fused in a platinum crucible, and powdered in an agate mortar. The constants of the Hartley cells were 0·022996 (large) and 0·037351, and of the small cell 0·19094. The values of the cell constants were redetermined at frequent intervals and were found not to alter appreciably subsequently to the first month after manufacture. Experiments were also carried out to determine the influence of the volume of the solution in the cell on the cell constants; no change was detected by the addition of quantities of 0·01*N*-potassium chloride solution comparable with those added in the runs.

Preparation of the solutions. The solutions were made up in 125 or 250 c.c. wide-necked Pyrex flasks with ground glass stoppers. The substance was weighed out in a small platinum crucible or a small Pyrex weighing-bottle—not less than 1 g. being usually employed—and transferred to the stoppered glass flask containing a known weight of conductivity water of the same sample as that used in filling the cell.

The *weight pipette* had a capacity of about 20 c.c. and was fitted with a small tap, lubricated with pure vaselin, the lower end of which was connected to a capillary tube, 4 cm. long, covered at its extreme end by a small ground-glass cap. The top of the pipette was fitted with a ground glass cap carrying a fine capillary tube 1 cm. long. Two glass hooks were fused into the body of the pipette; these served the double purpose of handling and of providing a means of suspension by a silver wire. The pipette was filled by dipping the lower end beneath the surface of the stock solution contained in the wide-mouthed flask, and applying suction to the upper capillary. The upper cap was not removed during an experiment; the lower cap was removed only during the additions. During the addition of the stock solution from the weight pipette, a slow stream of dry, carbon dioxide-free air was passed into the cell through the three-way tap attached to the main cap of the cell to prevent the absorption of atmospheric impurities.

Conductivity measurements. Before each series of measurements the cells, weight pipettes, and weighing-bottles were allowed to stand for at least 24 hours with chromic–concentrated sulphuric acid mixture, thoroughly washed with distilled water, steamed out for at least 6 hours with steam generated from distilled water, and washed with conductivity water. The cells were then thoroughly washed with redistilled absolute alcohol and dried by drawing a current of carbon dioxide-free, dry air through them for about 24 hours. The other apparatus was dried in the steam-oven and allowed to cool in a vacuum desiccator over calcium chloride or phosphoric oxide. This procedure was adopted between each series of conductivity measurements. The electrodes were always kept short-circuited except during the actual measurements, as recommended by Morgan and Lammert (*J. Amer. Chem. Soc.*, 1923, **45**, 1692). During the conductivity measurements, the bridge was approximately set and the current switched off for 5 to 10 minutes : the final setting was made in about 2 seconds. Three readings, for three values of resistance, were taken at each concentration. Perfect minima were always obtained, and the bridge could be set to 0·01% of its length. Two experiments, with different stock solutions, were generally made for each substance; it was usual to make nine additions in each series of measurements.

Calculation of the concentrations. All the concentrations are expressed in g.-mols. per litre of solution at 25°. In the first instance the concentrations are known in weight normalities and in order to convert them into volume normalities, the density at 25° of the final solution in the cell was determined in each experiment with a carefully calibrated pyknometer and a linear variation of density with concentration was assumed.

Solvent correction. The conductivity of the water, as determined by the small cell, was subtracted from the total conductivity at each concentration. This correction was applied to both the salts and the acids. For the latter the correction amounted to about 2% of the total conductivity at a concentration of 10^{-4} molar, and decreased rapidly with increase of concentration and was usually less than 0·1% at a concentration of *ca.* 10^{-2} molar. No maximum in the conductivity–concentration curve was observed in dilute solutions of the acids (compare Whetham, *Z. physikal. Chem.*, 1906, **55**, 204; Whetham and Paine, *Proc. Roy. Soc.*, 1908, *A*, **81**, 58; Paine and Evans, *Proc. Camb. Phil. Soc.*, 1914, **18**, 1; Kendall, *J. Amer. Chem. Soc.*, 1917, **39**, 7).

Results.

The results are collected in the following tables and are expressed in the manner widely employed by Kohlrausch ("Gesammelte Abhandlungen," 1911). C is the concentration in g.-mols. per litre, κ is the specific conductivity of the solvent, μ is the molecular conductivity, and K_1 is the primary dissociation constant. In order to economise space, the actual experimental results will be given for only two acids, *viz.*, malonic and methylmalonic acids; one experiment each for disodium ethyl-*n*-propyl- and di-*n*-propyl-malonates is also included as illustrative of the type of results obtained with the disodium salts. These are given in Table I. Table II contains the values at round concentrations, interpolated from a large-scale conductivity–concentration curve, of μ, of $\alpha = \mu/\mu_0$, where μ_0 is the molecular conductivity at infinite dilution of the acid ionising as a uni-univalent electrolyte (*vide* p.

Table I.

Malonic acid.

	$C \times 10^4$.	μ.		$C \times 10^4$.	μ.
Series (a) *	0·4098	369·2	Series (c) *	17·392	226·0
$\kappa \times 10^7$, 9·025	2·0024	337·6	$\kappa \times 10^7$, 8·872	27·244	201·5
	5·2031	298·2		39·068	180·0
	7·9251	275·0		52·070	163·2
	12·097	249·3		64·770	151·1
	18·798	221·0		77·904	139·8
Series (b) †	2·0068	340·4	Series (d) *	1·3173	347·2
$\kappa \times 10^7$, 9·003	4·0083	313·3	$\kappa \times 10^7$, 8·934	4·8317	301·2
	6·9827	284·3		15·833	234·1
	13·601	243·3		32·637	191·0
	24·540	206·5		48·090	168·9
				74·165	142·8
				96·422	128·1

Methylmalonic acid.

	$C \times 10^4$.	μ.		$C \times 10^4$.	μ.
Series (a) *	0·4713	382·7	Series (b) *	0·6669	372·7
$\kappa \times 10^7$, 8·454	1·1866	348·2	$\kappa \times 10^7$, 8·953	1·6586	333·0
	2·2686	318·8		9·1928	234·8
	6·3364	260·0		17·361	192·8
	15·611	199·6		29·307	162·0
	27·728	165·8		43·127	139·6
	39·563	145·5		56·552	126·1
	52·246	130·3		76·995	111·1
	76·995	111·4			

Disodium ethyl-*n*-propylmalonate.			Disodium di-*n*-propylmalonate.		
Series (a) *	1·9889	186·9	Series (a) *	1·7115	182·3
$\kappa \times 10^7$, 8·934	3·8190	185·7	$\kappa \times 10^7$, 9·838	4·4683	180·5
	6·5738	183·9		8·9771	177·7
	9·7414	181·9		12·979	175·8
	14·355	179·3		18·783	172·9
	20·527	176·7		27·196	169·7
	27·318	174·3		35·887	166·6
	38·688	170·9			

* Cell constant, 0·022996. † Cell constant, 0·037351.

1476), and of K_1 for malonic and methylmalonic acids. The results for the remaining six acids have been incorporated in Table III, which contains the similarly interpolated values of the molecular conductivity—in every case a smooth curve could be drawn without ambiguity through the experimental results—at concentrations greater than 1×10^{-3} molar. Table IV contains the results for these acids at round concentrations from $C = 1 \times 10^{-4}$ to $C = 1 \times 10^{-3}$ molar.

TABLE II.

	Malonic acid.			Methylmalonic acid.		
$C \times 10^4$.	μ.	α.	$K_1 \times 10^4$.	μ.	α.	$K_1 \times 10^4$.
1	356·5	0·874	6·06	353·8	0·875	6·14
2	338·6	0·830	8·11	325·4	0·805	6·65
5	300·8	0·738	10·36	274·9	0·680	7·23
10	261·7	0·642	11·48	229·7	0·568	7·48
20	219·0	0·537	12·45	183·8	0·455	7·58
30	195·5	0·479	13·24	160·8	0·398	7·88
40	179·2	0·439	13·77	144·7	0·358	7·98
50	166·7	0·409	14·12	132·3	0·327	7·96
60	155·8	0·382	14·16	123·0	0·304	7·99
70	146·5	0·359	14·09	115·4	0·286	7·99
80	138·7	0·340	14·02	109·3	0·270	8·03

Malonic acid: $\mu_0 = 407{\cdot}9$. $K_1 = 1{\cdot}410 \times 10^{-3}$.

Methylmalonic acid: $\mu_0 = 404{\cdot}2$. $K_1 = 7{\cdot}99 \times 10^{-4}$.

TABLE III.

	Dimethylmalonic acid.		Ethylmalonic acid.		Methylethylmalonic acid.	
	$\mu_0 = 398{\cdot}4$.		$\mu_0 = 398{\cdot}3$.		$\mu_0 = 397{\cdot}3$.	
$C \times 10^3$.	μ.	$K_1 \times 10^4$.	μ.	$K_1 \times 10^4$.	μ.	$K_1 \times 10^4$.
2	168·8	6·23	197·5	9·75	218·2	13·38
3	146·4	6·40	174·4	10·23	191·6	13·48
4	132·0	6·57	157·7	10·38	174·7	13·80
5	120·6	6·57	144·4	10·31	161·2	13·85
6	111·8	6·57	134·0	10·23	150·9	13·94
7	104·8	6·57	126·0	10·25	142·0	13·92
8	99·0	6·57	119·7	10·33	134·8	13·94
9	94·1	6·57	114·0	10·33	128·6	13·92
	$K_1 = 6{\cdot}57 \times 10^{-4}$.		$K_1 = 1{\cdot}030 \times 10^{-3}$.		$K_1 = 1{\cdot}394 \times 10^{-3}$.	

	Diethylmalonic acid.		Ethyl-*n*-propyl-malonic acid.		Di-*n*-propyl-malonic acid.	
	$\mu_0 = 396{\cdot}85$.		$\mu_0 = 392{\cdot}2$.		$\mu_0 = 389{\cdot}65$.	
$C \times 10^3$.	μ.	$K_1 \times 10^3$.	μ.	$K_1 \times 10^3$.	μ.	$K_1 \times 10^3$.
2	310·7	5·65	312·8	6·28	315·0	6·82
3	291·4	6·09	294·7	6·81	298·7	7·55
4	275·5	6·30	280·0	7·12	284·4	7·89
5	261·8	6·39	267·3	7·29	272·4	8·12
6	249·5	6·39	256·0	7·36	262·1	8·29
7	239·0	6·38	246·0	7·39	253·0	8·42
8	—	—	236·8	7·36	245·3	8·56
	$K_1 = 6{\cdot}39 \times 10^{-3}$.		$K_1 = 7{\cdot}37 \times 10^{-3}$.		$K_1 =$ *ca.* 9×10^{-3} (?)	

TABLE IV.

	Dimethylmalonic acid.		Ethylmalonic acid.		Methylethylmalonic acid.	
$C \times 10^4$.	μ.	$K_1 \times 10^4$.	μ.	$K_1 \times 10^4$.	μ.	$K_1 \times 10^4$.
1	330·6	4·05	334·0	4·36	334·5	4·48
2	298·8	4·50	317·0	6·21	322·3	6·97
5	254·1	5·62	279·8	8·29	294·0	10·53
10	213·8	6·22	238·3	8·91	260·7	12·53

	Diethylmalonic acid.		Ethyl-*n*-propylmalonic acid.		Di-*n*-propylmalonic acid.	
$C \times 10^4$.	μ.	$K_1 \times 10^3$.	μ.	$K_1 \times 10^3$.	μ.	$K_1 \times 10^3$.
1	—	—	366·3	1·32	—	—
2	362·9	1·96	362·3	2·24	357·0	2·00
5	351·8	3·46	351·4	3·86	347·8	3·71
10	336·0	4·67	336·0	5·12	334·8	5·25

TABLE V.

Disodium salts.

	Malonate.	Methylmalonate.	Dimethylmalonate.	Ethylmalonate.
$C \times 10^4$.	μ.	μ.	μ.	μ.
2	219·0	209·5	200·2	200·4
5	217·1	206·5	198·5	199·0
10	214·2	202·6	195·8	196·9
20	209·4	196·8	191·0	193·1
30	205·3	192·6	186·9	189·8
35	203·6	190·9	185·1	188·3
40	201·9	189·4	183·4	—
	μ_0 220·55	213·1	201·5	201·3

	Methylethylmalonate.	Diethylmalonate.	Ethyl-*n*-propylmalonate.	Di-*n*-propylmalonate.
$C \times 10^4$.	μ.	μ.	μ.	μ.
2	196·7	197·1	187·0	182·1
5	194·2	195·6	184·8	180·1
10	190·8	193·4	181·7	177·2
20	185·8	189·7	176·8	170·4
30	182·3	186·8	173·2	168·5
35	181·0	185·6	171·8	166·8
40	179·8	—	170·6	—
	μ_0 199·3	198·4	189·1	184·0

The molecular conductivities at round concentrations for the disodium salts are collected in Table V, together with the values of μ_0, the molecular conductivity at infinite dilution, computed by Ferguson and Vogel's method (*vide infra*). The conductivities of the disodium salts decrease with decrease in concentration below 2×10^{-4} molar.

The results for sodium hydrogen malonate, which was prepared by mixing equivalent weights of malonic acid and anhydrous sodium malonate, are given in Table VI : $M = 126{\cdot}02$.

TABLE VI.

Sodium hydrogen malonate.

$C \times 10^4$	1	2	[illegible]	10	20	30
μ	192·0	178·0	[illegible]	107·4	97·4	94·1
$C \times 10^4$	40	50	60	70	80	
μ	91·9	90·3	88·9	87·9	86·9	

Discussion and Calculation of the Dissociation Constants.

The ionisation of a dibasic acid H_2X may be assumed to take place in two stages :

$$H_2X \rightleftharpoons HX^- + H^+ \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$HX^- \rightleftharpoons X^{--} + H^+ \quad . \quad . \quad . \quad . \quad . \quad (2)$$

leading to the primary dissociation constant

$$K_1 = [HX^-][H^+]/[H_2X] \quad . \quad . \quad . \quad . \quad . \quad (1')$$

and the secondary dissociation constant

$$K_2 = [X^{--}][H^+]/[HX^-] \quad . \quad . \quad . \quad . \quad . \quad (2')$$

if it be assumed that dissociation is incomplete and the law of mass action applies. If μ_0 = molecular conductivity at infinite dilution of the acid H_2X, ionising according to equation (1), then $\mu_0 = l_{HX^-} + l_{H^+}$ where l_{HX^-} and l_{H^+} represent the mobilities or ionic conductivities at infinite dilution of the HX^- and H^+ ions, respectively. The most probable value for l_{H^+} as evaluated by Ferguson and Vogel (*Phil. Mag.*, 1927, **4**, 300) from the data of Kraus and Parker (*J. Amer. Chem. Soc.*, 1922, **44**, 2429) on iodic acid and of Parker (*ibid.*, 1923, **45**, 2017) on hydrochloric acid is 349·05 at 25°. Unfortunately, l_{HX^-} cannot be computed from the conductivity data of sodium hydrogen salts, as will be evident from the results for sodium hydrogen malonate in Table VI, owing to the manifestation of secondary ionisation in dilute solutions. The method adopted in the present paper is as follows : The value of μ_0 for the disodium salt, Na_2X, was computed by the graphical method of Ferguson and Vogel (*Phil. Mag.*, 1925, **50**, 971) by means of the equation

$$\mu_0 = \mu + bC^n.$$

This formula was valid up to a concentration of the order of 2×10^{-3} molar. By subtracting twice the mobility of the sodium ion, $2l_{Na^+}$, which was taken as 51·4 (Ferguson and Vogel, *Phil. Mag.*, 1927, **4**, 233), the ionic conductivity of the ion X^{--} is obtained. l_{HX^-} was assumed equal to $0{\cdot}5l_{X^{--}}$. Experimental support for this assumption is provided by the extensive conductivity measurements on the sodium hydrogen and disodium salts of dibasic acids by Chandler (*J. Amer. Chem. Soc.*, 1908, **30**, 694) in which the molecular conductivity of the disodium salt is approximately twice that of the sodium hydrogen salt over a [illegible]ly wide range of concentration. Knowing μ_0 and assuming α [illegible]$/\mu_0$, $K_1 = \alpha^2 C/(1 - \alpha)$, where C is the concentration.

The secondary ionisation co[illegible]ant cannot at present be calculated without ambiguity from con[illegible]tivity data (compare Wegscheider, *Monatsh.*, 1902, **23**, 599), nor is there any trustworthy evidence that the secondary ionisation of the malonic acids conforms to the mass-action law. It is proposed to discuss the question more fully in a future communication, but it will suffice here to state that, although some eight methods have now been employed for the determination of secondary ionisation constants, it cannot be said that the secondary ionisation constant of any dibasic acid is known with an accuracy approaching 10%.

Inspection of the tables reveals the following facts. When the value of α falls below 0·3—0·4 for malonic, methyl-, ethyl-, dimethyl-, and methylethyl-malonic acids and below 0·6—0·7 for diethyl- and ethyl-*n*-propyl-malonic acids, the acids seem to ionise as uni-univalent electrolytes. Di-*n*-propylmalonic acid appears to behave as a so-called strong electrolyte, since there is no evidence of a primary dissociation constant over the whole of the concentration range studied.

The diminution of K_1 with decrease of concentration at low concentrations is an outstanding feature of the results. No definite explanation of this anomaly is offered at present, although it is possible that the secondary ionisation of the malonic acids does not conform to the simple mass-action law, *i.e.*, K_2 does not exist.

A conspectus of the results is exhibited in Tables VII and VIII.

TABLE VII.

Acid.	μ_0.	$K_1 \times 10^4$.
Malonic	407·9	14·10
Methylmalonic	404·2	7·99
Ethylmalonic	398·3	10·30
Dimethylmalonic	398·4	6·57
Methylethylmalonic	397·3	13·94
Diethylmalonic	396·85	63·9
Ethyl-*n*-propylmalonic	392·2	73·7
Di-*n*-propylmalonic	389·65	*ca.* 90 (?)

TABLE VIII.

Disodium salt.	μ_0.	$l_{\mathrm{X}^{--}}$.	b.	n.
Malonate	220·55	117·7	2071	0·8387
Methylmalonate	213·1	110·3	961	0·6551
Ethylmalonate	201·3	98·5	2643	0·9271
Dimethylmalonate	201·5	98·7	2978	0·9085
Methylethylmalonate	199·3	96·5	1115	0·7080
Diethylmalonate	198·4	95·6	1416	0·8185
Ethyl-*n*-propylmalonate	189·1	86·3	1424	0·7619
Di-*n*-propylmalonate	184·0	81·2	1170	0·7917

In the first place it will be seen that the effect of successively substituting methyl groups for the two hydrogen atoms of malonic acid is a lowering of the dissociation constant, whereas the substitution of larger groups causes an increase. There can be no question that at least two factors come into play, *viz.*, the polar factor by virtue of the charge associated with the alkyl group, and the volume factor. The remarkable difference in dissociation constants between methylethyl- and diethyl- and the higher substituted malonic acids is noteworthy; this may have some theoretical significance. The values of μ_0 for the disodium salts decrease with increasing substitution; isomeric ions such as those of ethyl- and dimethyl-malonic acids have the same mobility.

No account has been taken in the present calculations of the influence of interionic attractions and related effects; it is hoped to discuss the question more fully in a future communication (compare Sherrill and Noyes, *J. Amer. Chem. Soc.*, 1926, **48**, 1861; MacInnes, *loc. cit.*, p. 1861).

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