CCXXIV.—*Electrometric Titration Curves of Dibasic Acids. Part III. Substituted Malonic Acids.*

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IN our preliminary survey (J., 1928, 1594) of the possibility of measuring the distance between the carboxyl groups of a dibasic acid by utilising hydrogen potentials during neutralisation in conjunction with Bjerrum's theory concerning the effect of an ionic centre on local hydrogen-ion concentration, we suggested that two important disturbing factors would require recognition when interpreting results obtained by this method.

One is due to solvation and electrostriction, which should render the estimated distances too large. This disturbance is expected to be almost universal, and hence difficult to eliminate by any experimental means; nevertheless, it should depend mainly on the conditions of measurement, and, for a series of related acids, measured in the same way, should be largely independent of the acid, even although the estimated distances might not be physically exact. A simple illustration of this effect disclosed itself during our examination (*loc. cit.*) of the homologous normal dibasic acids from glutaric acid to azelaic acid. Katz's recent investigation, by *X*-ray methods, on the shape and arrangement of molecules in the liquid state (*Z. angew. Chem.*, 1928, **41**, 329) indicates a straight configuration (with zig-zags) for those types of normal-chain molecules which are known (Müller, Shearer) to assume this configuration in the crystal, and Caspari has lately shown (J., 1928, 3235) that the normal dibasic acids assume the straight configuration in the crystal, the increment in the length of the chain for each additional methylene group being about 1·26 Å.U. Our investigation also has revealed a constant increase in the length of the chain for each added methylene group; but the value of the increment was 1·73 Å.U., indicating that all the estimated distances are increased in this proportion by the effect under discussion. Since the conditions of these measurements have been repeated in the present work, the same consideration will apply. It corresponds to an effective reduction, attributable to solvation, amounting to about 17% in the external field of the carboxylate ion.

The second source of disturbance is that which arises from internally propagated polar influences; and in dibasic acids the effect of the inductively propagated electron-attraction of one carboxyl group on the ionisation of the other is of particular importance : it tends to make the determined distances too small. It is known, however, that even the most powerful polar influences, when relayed by induction along a chain of methylene groups, rapidly become damped out; for instance, in aromatic substitution, the *m*-orienting effect of the ammonium pole, although large in benzylammonium compounds, is smaller in their β-phenylethyl-, and almost inappreciable in their γ-phenylpropyl-analogues (Goss, Ingold, and Wilson, J., 1926, 2440; Goss, Hanhart, and Ingold, J., 1927, 250; Ingold and Wilson, J., 1927, 810). Similarly, our investigation (*loc. cit.*) of the acids $CO_2H{\cdot}[CH_2]_n{\cdot}CO_2H$ showed that, whilst malonic acid exhibits a large anomaly of the expected type, with succinic acid the effect is smaller, and with glutaric acid it is negligible; that is to say, transmission through three methylene groups suffices practically to destroy the inductive effect of the carboxyl group. Furthermore, in an experimental comparison of alkylated dibasic acids (such as those used in the present work) the inductive polar effect due to the replacement of hydrogen by alkyl may assume significance; but this internal polar influence is known from independent evidence relating to addition and elimination reactions (Lucas and Moyse, *J. Amer. Chem. Soc.*, 1925, **47**, 1459; Lucas, Simpson, and Carter, *ibid.*, p. 1462; Hanhart and Ingold, J., 1927, 997; Ingold and Vass, J., 1928, 3125; Fenton and Ingold, forthcoming paper) to be so much weaker than that of carboxyl that it would almost certainly be reduced to negligible dimensions after transmission through two carbon atoms. Thus it should be possible, by avoiding alkyl substituents too near the carboxyl groups and a too great proximity of these groups, to obtain examples substantially free from internal polar disturbances; and this we have demonstrated (J., 1928, 2267) by showing that a long series of β-alkylated glutaric acids (in which the carboxyl groups should be sufficiently far apart and the alkyl groups sufficiently distant from both to secure the desired simplification) are placed by measurements of the apparent distance between the carboxyl groups in precisely the order indicated by the numerous chemical relationships summarised in the hypothesis of valency deflexion. Not only does the order agree, but also the gaps between the successive members of the series are related in the expected manner, thus confirming the conclusions already indicated regarding the conditions for the practical elimination by damping of the internally transmitted polar effects of carboxyl and alkyl.

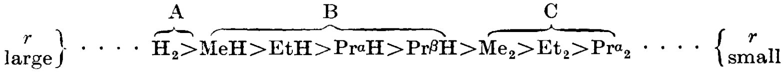
In these examples we circumvented the solvation disturbance by treating the results comparatively, and avoided the internal polar factor by a special choice of structure, thus, as it were, isolating the spatial relations. In developing these studies it seemed that the next case in order of complexity would be one in which the polar factor also is allowed effectively to enter, and we therefore turned to the alkylated malonic acids. The anticipated consequence was not confusion, because sufficient is known of the polarity of carboxyl and alkyl groups largely to exclude an arbitrary or indefinite interpretation. We have followed our former plan for dealing with the solvation factor.

The data recorded in the experimental portion lead to the following values of the apparent distance (r) between the carboxyl groups of the malonic acids $CRR'(CO_2H)_2$. The distances are in Ångström units.

RR'	H_2	Me,H	Et,H	Pr^{α},H	Pr^{β},H	Me_2	Et_2	Pr_2^{α}
r	1·54	1·64	1·50	1·47	1·37	1·45	0·71	0·64

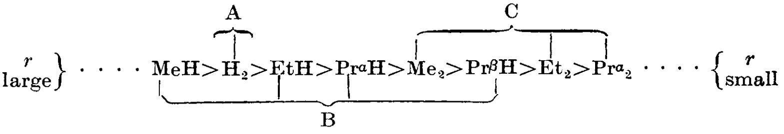
It is necessary now to consider to what extent the results accord with the considerations outlined in the foregoing paragraphs.

(a) *The Order of the Compounds.*—For reasons already indicated we shall assume that solvation augments the measured distance, that the inductive electron-attraction of the carboxyl groups diminishes it, and that these effects are nearly constant throughout the series studied. It is the internal polar influence of the alkyl groups on the carboxyl groups that should constitute the main *variable* disturbance to a series of results which otherwise ought to correspond to the normal spatial relations. These spatial relations, expressed in the hypothesis of valency deflexion, would place the compounds in the following order :



$$\left.\begin{matrix} r \\ \text{large}\end{matrix}\right\} \cdots\cdot \overbrace{\mathrm{H_2}}^{\text{A}}>\overbrace{\mathrm{MeH}>\mathrm{EtH}>\mathrm{Pr^{\alpha}H}>\mathrm{Pr^{\beta}H}}^{\text{B}}>\overbrace{\mathrm{Me_2}>\mathrm{Et_2}>\mathrm{Pr^{\alpha}_2}}^{\text{C}} \cdots\cdot \left\{\begin{matrix} r \\ \text{small}\end{matrix}\right.$$

Now the inductive effect of replacing hydrogen by alkyl is to depress the ionisation of the malonic acid molecule; but in the hydrogen malonate ion the inductive effect of the negative pole will reduce or reverse the polarity of the alkyl substituent, wherefore the internal polar influence of this substituent on the ionisation of the anion should be reduced or inverted; and this combination of effects is equivalent to an increase in the estimated distance r. Furthermore, we have given reasons for assuming that the polar effect of replacing hydrogen by alkyl will become insignificant at the carboxyl groups after transmission through two intervening carbon atoms; and since, in the above series of acids such an effect is never transmitted through less than one intermediate carbon atom, it follows that only the first carbon atom of each alkyl group (in other words, only the β-carbon atoms of the acids) need be counted as contributing to the variable polar factor. The disturbance created by this factor should, therefore, take the following form : (1) the members of group B in the above series should suffer no disarrangement amongst themselves; (2) the same should apply to members of group C; but, (3) group B as a whole (one β-carbon atom) should undergo displacement to the left in the series relatively to A (no β-carbon atom); and (4) group C as a whole (two β-carbon atoms) should be displaced to the left relatively to the new position of group B. The determined order bears this out :



$$\left.\begin{matrix} r \\ \text{large}\end{matrix}\right\} \cdots\cdot \underbrace{\mathrm{MeH}>\overbrace{\mathrm{H_2}}^{\text{A}}>\mathrm{EtH}>\mathrm{Pr^{\alpha}H}>\mathrm{Me_2}>\mathrm{Pr^{\beta}H}}_{\text{B}}>\overbrace{\mathrm{Et_2}>\mathrm{Pr^{\alpha}_2}}^{\text{C}} \cdots\cdot \left\{\begin{matrix} r \\ \text{small}\end{matrix}\right.$$

(b) *The Relative Intervals.*—The general theory relating to the structural influences considered above may be correlated somewhat more precisely with the actual numerical results by examining the differences between the figures for the various members of the series taken in pairs. The following are some obvious theoretical requirements. The interval between the recorded distances for methyl- and ethyl-malonic acid should not be very different from the corresponding interval for ethyl- and *iso*propyl-malonic acid, since each difference depends on the same structural change, *i.e.*, the same substitution in the same position relative to the carboxyl groups, in structurally similar parents. Each of these intervals should exceed that given by ethyl- and *n*-propyl-malonic acids, since this last difference depends on a similar substitution in a more remote position from the carboxyl groups. The disparity between the distances for the dimethyl- and diethyl-acids should exceed that shown by the diethyl- and di-*n*-propyl-acids, and should do so by a greater ratio than that of the preceding comparison, because the reason there given applies twice over in the present case. The interval for the dimethyl- and diethyl-acids should also exceed those shown by the methyl- and ethyl-acids and by the ethyl- and *iso*-propyl-acids, because the structural difference represented in the last two pairs of acids is present also in the first pair, together with an additional difference of the same kind. For similar reasons, the difference exhibited by the diethyl- and di-*n*-propyl-acids should exceed that shown by the ethyl- and *n*-propyl-acids. The extent to which these theoretical deductions, which are based wholly on considerations of valency deflexion, accord with the values obtained by observation is shown in the following table, from which it will be seen, not only that all the differences are in the right direction, but also that the ratios of the differences are divisible into fairly distinct groups corresponding with the prediction : the presumed identity in order of magnitude is represented by a ratio which is very nearly 1 ; the series of minor inequalities by a group of ratios falling between the limits 2 and 6, and the major inequality by the ratio 11.

	Predicted relation between intervals.			Observed differences (Å.U.).		Ratio
No.	Interval I.		Interval II.	Interval I.	Interval II.	I/II.
1	MeH–EtH	$\approx$	EtH–$\mathrm{Pr^{\beta}H}$	0·14	0·13	1
2	$\mathrm{Me_2}$–$\mathrm{Et_2}$	$>$	MeH–EtH	0·74	0·14	5
3	$\mathrm{Me_2}$–$\mathrm{Et_2}$	$>$	EtH–$\mathrm{Pr^{\beta}H}$	0·74	0·13	6
4	$\mathrm{Et_2}$–$\mathrm{Pr^{\alpha}_2}$	$>$	EtH–$\mathrm{Pr^{\alpha}H}$	0·07	0·03	2
5	MeH–EtH	$>$	EtH–$\mathrm{Pr^{\alpha}H}$	0·14	0·03	5
6	EtH–$\mathrm{Pr^{\beta}H}$	$>$	EtH–$\mathrm{Pr^{\alpha}H}$	0·13	0·03	4
7	$\mathrm{Me_2}$–$\mathrm{Et_2}$	$\gg$*	$\mathrm{Et_2}$–$\mathrm{Pr^{\alpha}_2}$	0·74	0·07	11

* The presumed structural cause of inequality No. 5 here applies twice.

Electrolytic Dissociation Constants.—Only minor modifications should be necessary in order to transform the substance of the above discussion of the *r*-values of dibasic acids into an analogous interpretation of their electrolytic dissociation constants, with which, of course, the *r*-values are closely connected in the Bjerrum theory. We have, for instance, disregarded an expected small alternating effect depending on the zig-zags of the alkyl groups. Small alternations are discernible amongst the dissociation constants of several series of aliphatic acids, and are probably to be regarded as a combined spatial-polar influence closely similar in orgin to what has been called the " direct effect " (Ingold and Vass, J., 1928, 417, 2262; Ingold and Ingold, J., 1928, 2249) in its application to aromatic substitution. Of the various factors of disturbance anticipated in our first paper (*loc. cit.*) this is the only remaining one, but its influence in the cases now considered should be small, if analogy with aromatic substitution can be taken as a guide. Furthermore, this factor, like all the variable polar disturbances (*i.e.*, those due to the alkyl groups), should be less prominent in the *r* values, and still less prominent in the second dissociation constants of the malonic acids, than in their first dissociation constants, partly owing to the suppression of normal alkyl polarity by the negative pole in the univalent anion, which reduces the effect on the second dissociation constant, and partly because polar disturbances enter into the *r*-values as a kind of mean between those which affect the two dissociation constants separately : in symbols, $\Delta(K_1)>\Delta(r)>\Delta(K_2)$, where the parentheses denote functions of structure, and the Δ's, generalised polar differentials. Thus the qualitative relationship between the dissociation constants of malonic acid and its alkyl derivatives should be as follows. Starting with the normal spatial sequence (illustrated on p. 1694), applied in accordance with the view that, owing to the proton-repulsion of carboxyl and the proton-attraction of carboxylate ion, the local hydrogen-ion concentrations will be changed in such a way that proximity of the carboxyl groups of an acid will lead to a high K_1 and a low K_2, then, *as regards* K_1, we can assert that the polar displacement of the groups of acids B and C to the left in the series will be more pronounced than was found for the *r*-values, and larger for C than for B, and that, if alternation is discernible (which it seems to be), it should be more apparent amongst the members of Group B, in which the spatial intervals are small, than amongst the *gem*-compounds of group C in which, for reasons already given, these intervals are larger; and, *as regards* K_2, we expect comparatively little polar disturbance amongst the groups A, B, and C, and no perceptible alternation.

The values of K_1 and K_2, calculated from our electrometric determinations, are given in the first table in the experimental section, and a brief examination of the figures will show that all the above conclusions are justified. Considering, for instance, the order of the compounds in ascending values of K_1, it is observed that the group of acids B has passed completely over to the left of A, and that the first member of group C has attained a position to the left of both groups A and B. Again, in the B-series there is a small apparent alternation ($K \times 10^4$ for Me-, Et-, Pr^{α}-acids $= 11, 13, 11$, respectively), but it cannot be perceived in the more spread-out values of the C-series ($K \times 10^4$ for Me_2-, Et_2-, Pr^{α}_2-acids $= 8, 62, 87$, respectively). Particularly evident is the fact that all the second dissociation constants follow the unaltered spatial sequence, although the presence of a small polar disturbance (of the expected kind) can be perceived by a study of the relative intervals. Thus the figures for the Me_2- and $Pr^{\beta}H$-acids show that the C-series has only just missed overlapping the B-series. Of course, owing to the special way in which concentrations and activities enter into the constitution of these constants, they are not likely to be identical with those which might be obtained by conductivity, partition, or catalysis (compare Part I, *loc. cit.*); nevertheless, the dissociation constants determined by any other single method should show a similar agreement with the theoretical requirements.*

We have given these applications of established principles more fully than would otherwise have been thought necessary because misapprehension appears still to exist regarding the point of view which actuates modern researches on the spatial influences expressed by valency deflexion. Hückel has commented on the anomalies presented by the malonic acids, but his view, that the recognition of polar influences is an arbitrary escape from difficulty, seems scarcely fair; it is, however, less remarkable than that of Lowry (*Chem. and Ind.*, 1928, **47**, 1150), who, whilst not disputing the contended superposition of polar influences, asserts that the hypothesis of valency deflexion " would lose most of its value if it could only be used as subsidiary to a major hypothesis of polarity." Our view is, and always has been, that a competent *general* theory of reactivity cannot neglect either the spatial or the polar factor, and

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* A new series of determinations of K_1 by conductivity of certain alkylated malonic acids has appeared as the proofs come to hand (Vogel, this vol., p. 1476). The selection of examples differs somewhat from ours, but the data are in excellent agreement with the considerations outlined above. The order is

$$\left.\begin{matrix}K_1\\ \text{small}\end{matrix}\right\} \cdots \underbrace{\mathrm{Me_2}<\overbrace{\mathrm{MeH}<\mathrm{EtH}}^{B}<\overbrace{\mathrm{H_2}}^{A}<\mathrm{MeEt}<\mathrm{Et_2}<\mathrm{EtPr^{\alpha}}<\mathrm{Pr^{\alpha}_2}}_{C} \cdots \left\{\begin{matrix}K_1\\ \text{large}\end{matrix}\right.$$

and it will be noticed that the two members of Group C fit into their proper places.

that which is " major " and which " subsidiary " in a given case depends entirely on the structural circumstances of that case. In the studies now described it would be hard to say—each factor plays its part.

EXPERIMENTAL.

The substituted malonic acids were either purchased or prepared by known methods, and in all cases carefully purified by repeated crystallisation before use. The hydrogen-potential measurements were carried out and standardised, and the results calculated, just as described in Part I (*loc. cit.*). The titres recorded below are in c.c. and the *E.M.F.*'s in volts.* The remaining data necessary for the application of the Auerbach–Smolczyk equation are recorded in the second, third, and fourth columns of the table immediately following. The calculated values of K_1 and K_2 are in the fifth and sixth columns; they refer to the temperature 25°, at which all the hydrogen-potential determinations were carried out.

RR′ in acid RR′C(CO$_2$H)$_2$.	Original conc., *M* (mols./l.).	Conc. of NaOH (*N*).	Equivalent titre (c.c.).	$K_1 \times 10^4$.	$K_2 \times 10^7$.
H$_2$	0·04991	1·116	13·42	17·7	43·7
MeH	0·05040	1·116	13·55	10·7$_5$	34·3
EtH	0·05905	1·596	11·10	12·6$_5$	28·1
Pr$^{\alpha}$H	0·01622	0·1116	43·63	10·7	20·8
Pr$^{\beta}$H	0·007665	0·1116	20·58	11·7	15·9
Me$_2$	0·05560	1·116	10·45	8·27	15·3
Et$_2$	0·006100	0·1116	16·42	62·3	0·590
Pr$^{\alpha}_2$	0·003811	0·1116	10·25	86·7	0·342

Methylmalonic Acid.—*E.M.F.* = 0·3733 at titre 0·0 and 0·6970 at titre 13·51.

Titre	0·00	0·50	1·02	1·77	2·70	4·00	5·02	5·78
p_H	2·173	2·305	2·435	2·616	2·827	3·150	3·431	3·694
Titre	6·28	6·76	7·15	8·00	9·00	10·00	11·03	11·98
p_H	3·950	4·232	4·462	4·862	5·179	5·430	5·687	5·972
Titre	13·08	13·16	13·30	13·51				
p_H	6·579	6·674	6·836	7·431				

Ethylmalonic Acid.—*E.M.F.* = 0·3710 at titre 0·0 and 0·8541 at titre 11·17.

Titre	0·00	0·25	0·48	0·88	1·32	1·78	2·27	2·88
p_H	2·132	2·205	2·269	2·389	2·520	2·653	2·789	2·956
Titre	3·35	3·75	4·20	4·62	4·98	5·18	5·50	5·90
p_H	3·092	3·221	3·392	3·571	3·773	3·911	4·181	4·553
Titre	6·21	6·61	7·01	7·42	7·78	8·29	8·70	9·15
p_H	4·762	4·965	5·130	5·272	5·388	5·536	5·660	5·807
Titre	9·56	9·98	10·60	10·74	10·83	10·87	10·92	11·17
p_H	5·956	6·136	6·524	6·682	6·815	6·895	6·994	10·310

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* Those for malonic acid itself are recorded in Part I. In the discussion of the theory of the method in Part I reference to Britton's paper (J., 1925, **127**, 1896) was inadvertently omitted.

n-*Propylmalonic Acid.*—*E.M.F.* = 0·3888 at titre 0·0 and 0·8179 at titre 43·73.

Titre	0·00	1·05	3·01	4·98	6·98	9·00	10·98	13·00
p_{H}	2·435	2·487	2·576	2·705	2·821	2·944	3·068	3·207
Titre	14·95	16·98	18·98	19·98	20·98	22·97	25·00	26·96
p_{H}	3·363	3·554	3·809	3·986	4·207	4·670	5·004	5·225
Titre	29·00	31·01	33·00	35·02	37·00	37·99	39·97	41·91
p_{H}	5·408	5·567	5·719	5·891	6·075	6·185	6·455	6·876
Titre	42·22	42·44	42·65	43·73				
p_{H}	6·959	7·066	7·191	9·698				

iso*Propylmalonic Acid.*—*E.M.F.* = 0·3980 at titre 0·0 and 0·8508 at titre 20·98.

Titre	0·00	0·23	0·73	1·19	1·62	2·99	4·00	4·99
p_{H}	2·591	2·616	2·662	2·701	2·739	2·871	2·990	3·093
Titre	6·00	7·96	8·99	9·98	10·50	10·98	11·45	11·97
p_{H}	3·221	3·548	3·814	4·340	4·540	4·777	4·964	5·127
Titre	12·50	12·97	14·00	14·99	15·99	17·00	18·00	19·00
p_{H}	5·260	5·363	5·553	5·717	5·881	6·058	6·259	6·529
Titre	19·50	19·65	19·74	19·98	20·08	20·64	20·73	20·98
p_{H}	6·682	6·802	6·856	7·014	7·117	9·428	9·798	10·250

Dimethylmalonic Acid.—*E.M.F.* = 0·3773 at titre 0·0 and 0·8623 at titre 10·51.

Titre	0·00	0·20	0·50	1·02	1·50	1·81	2·20	2·62
p_{H}	2·241	2·301	2·423	2·591	2·765	2·860	2·983	3·108
Titre	2·98	3·45	4·08	4·47	4·85	5·20	5·55	5·91
p_{H}	3·223	3·382	3·623	3·830	4·085	4·432	4·782	5·046
Titre	6·28	6·69	7·10	7·62	8·22	8·63	8·98	9·48
p_{H}	5·246	5·418	5·573	5·733	5·912	6·069	6·211	6·445
Titre	9·83	10·02	10·22	10·51				
p_{H}	6·674	6·852	7·169	10·440				

Diethylmalonic Acid.—*E.M.F.* = 0·3858 at titre 0·0 and 0·8389 at titre 16·78.

Titre	0·00	0·25	0·50	1·98	3·01	3·55	3·96	4·49
p_{H}	2·385	2·413	2·443	2·559	2·652	2·709	2·754	2·816
Titre	4·97	5·50	5·97	6·50	7·01	7·53	8·00	8·51
p_{H}	2·885	2·968	3·057	3·178	3·341	3·592	4·096	5·765
Titre	8·90	9·50	10·03	10·50	10·97	11·51	12·00	12·50
p_{H}	6·185	6·512	6·701	6·831	6·955	7·074	7·179	7·288
Titre	13·47	14·50	14·97	15·51	16·40	16·45	16·50	16·54
p_{H}	7·491	7·755	7·877	8·107	8·971	9·124	9·266	9·418
Titre	16·59	16·64	16·68	16·78				
p_{H}	9·587	9·731	9·850	10·050				

Di-n-*propylmalonic Acid.*—*E.M.F.* = 0·3960 at titre 0·0 and 0·8412 at titre 10·56.

Titre	0·00	0·52	1·05	1·55	2·01	2·50	3·00	3·51
p_H	2·551	2·593	2·652	2·713	2·780	2·858	2·956	3·077
Titre	4·00	4·47	4·78	5·10	5·30	5·50	5·91	6·26
p_H	3·249	3·501	3·791	4·782	5·957	6·342	6·735	6·937
Titre	6·74	7·22	7·75	8·22	8·91	9·17	10·16	10·20
p_H	7·144	7·319	7·494	7·658	7·893	8·005	8·928	9·034
Titre	10·25	10·29	10·34	10·39	10·42	10·47	10·52	10·56
p_H	9·172	9·309	9·485	9·637	9·764	9·900	10·012	10·090

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