28. *The Effect of Temperature on the Ionisation Constants of Some Dibasic Acids.*

By Islwyn Jones and F. G. Soper.

In Bjerrum's quantitative treatment (*Z. physikal. Chem.*, 1923, **106**, 219) of the relative ionisation constants of symmetrical dibasic acids, the potential at a distance r from an ionised carboxyl group was taken as $-q/\varepsilon r$, q being the electronic charge and ε the dielectric constant. More accurate treatment of the potential as a function of distance has been made by Ingold (J., 1931, 2179). Debye had obtained as a first approximation for the average moment of a molecule, $\overline{m}$, in the direction of an electric field, $\overline{m} = \gamma F + \mu^2 F/3kT$, where γ is the polarisability of the molecule and F the inner field acting on the molecule. This leads to the following expression connecting dielectric constant with electric moment :

$$(\varepsilon - 1)/(\varepsilon + 2) = 4\pi\nu(\gamma + \mu^2/3kT)/3 \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

If, however, the average moment of a molecule in the direction of the field is expanded to its next term,

$$\overline{m} = \gamma F + \mu^2 F/3kT - \mu^4 F^3/45k^3T^3 \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

the Clausius–Mosotti expression becomes

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{D - E}{D + 2E} = \frac{4\pi\nu}{3}\left[\gamma + \frac{\mu^2}{3kT} - \frac{1}{45}\frac{\mu^4 F^2}{k^3T^3}\right] \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where ν is the number of molecules per c.c., E the electric intensity, and D the induction at any point in the field. Ingold (*loc. cit.*) expressed E in terms of D by means of (3), expanded the expression in D as far as D^3, and replaced it by its equivalent q/r^2. In this way an expression for E was obtained as a function of r, and since potential, ϕ, is equal to $-\,dE/dr$, integration of the expression for E gave

$$\phi_1 = \frac{1 - \frac{4}{3}\pi\nu(\gamma + \mu^2/3kT)q}{1 + \frac{8}{3}\pi\nu(\gamma + \mu^2/3kT)r} + \frac{\frac{4}{5}\pi\nu\mu^4q^3/45k^3T^3}{[1 + \frac{8}{3}\pi\nu(\gamma + \mu^2/3kT)]^4r^5} \quad . \quad . \quad . \quad (4)$$

This may be compared with Bjerrum's expression where

$$\phi_B = q/\varepsilon r = [1 - \tfrac{4}{3}\pi\nu(\gamma + \mu^2/3kT)]/[1 + \tfrac{8}{3}\pi\nu(\gamma + \mu^2/3kT)]$$

Ingold further considered effects due to the compressibility of the solvent and to anisotropy, and derived numerical equations in which these effects are allowed for. These corrections, however, are of minor importance at distances of 4 Å. and over, as is shown by comparison of the values of ϕ_2, corrected for these other effects with those of ϕ_1, calculated from equation (4):

r, Å.	3·0	3·5	4·0	4·5	5·0	5·5	6·0	6·5	7·0
$\phi_1 \times 10^4$	7·67	4·35	2·86	2·10	1·66	1·38	1·19	1·06	0·952
$\phi_2 \times 10^4$ (Ingold)	6·73	4·17	2·83	2·08	1·65	1·38	1·19	1·06	0·952

Hence, when dealing with dibasic acids whose ionising centres are at distances apart of 4·0 Å. or more, we may ignore the corrections for anisotropy and compressibility without introducing appreciable error. It is thus possible, using (4), to obtain ϕ as a function of r at different temperatures, and so to obtain the distances apart of the ionising centres in the dibasic acid over a range of temperature.

In the evaluation of ϕ, the polarisability has been assumed to be independent of temperature, and μ has been evaluated from (1), ε being taken as $80 - 0\cdot4(t - 20°)$. This gives for $\mu \times 10^{18}$ at 25°, 50°, and 74°, the values 0·7611, 0·7920, 0·8220, respectively, and for the potentials

$$\begin{aligned}\phi_{25°} &= 6\cdot112 \times 10^{-12}/r + 1\cdot368 \times 10^{-41}/r^5\\ \phi_{50°} &= 7\cdot025 \times 10^{-12}/r + 1\cdot268 \times 10^{-41}/r^5\\ \phi_{74°} &= 8\cdot159 \times 10^{-12}/r + 1\cdot194 \times 10^{-41}/r^5 \quad . \quad . \quad . \quad . \quad . \quad (5)\end{aligned}$$

The value of the potential is obtained from Bjerrum's relation connecting the two ionisation constants of the acids, *viz.*, $\log K_1/K_2 - \log 4 = q\phi/2\cdot303kT$, and from this value of the potential, r is then obtained from (5).

In the present paper, the following symmetrical dibasic acids have been examined: *cis*- and *trans*-caronic, *cis*- and *trans*-hexahydroterephthalic, succinic, glutaric, β-methylglutaric, ββ-dimethylglutaric, β-*iso*propylglutaric, *cyclo*hexane-1 : 1-diacetic, adipic, *r*-βγ-diphenyladipic. The ionisation constants were determined electrometrically in cells without liquid junction (Harned and Robinson, *J. Amer. Chem. Soc.*, 1928, **50**, 3157), and the constants evaluated by the method of Kolthoff and Bosch (*Rec. trav. chim.*, 1928, **47**, 861).

EXPERIMENTAL.

The cell $H_2(Pt)|$Acid + NaOH, 0·001*M*-NaCl$|$AgCl,Ag was of a type already described (Jones and Soper, J., 1934, 1836). All silver–silver chloride electrodes were tested before use by immersion in *N*/10-potassium chloride solution connected with an *N*/10-calomel electrode, the *E.M.F.* of the resulting combination being 0·0451 ± 0·0002 volt at 25°. *E.M.F.* readings were corrected to a total pressure of 760 mm., *i.e.*, to a hydrogen pressure of $760 - p_{H_2O}$, where p_{H_2O} is the vapour pressure of water at the particular temperature. In order to convert *E.M.F.* readings into hydrogen-ion concentration, the *E.M.F.*, $E_{0\cdot001}$, of the cell $H_2(Pt)|0\cdot001M$-HCl$|$ Ag,AgCl was examined from 25° to 76·7° (Jones and Soper, *loc. cit.*), whence

$$-\log c_H = (E_1 - E_{0\cdot001})/0\cdot0001983T + 3\cdot000 + 2\log f_1/f_{0\cdot001}$$

The activity coefficients were evaluated at the required temperatures as previously described for tartaric acid (*loc. cit.*).

Results obtained in a typical series of experiments are given in the following table, the *E.M.F.* data referring to a temperature of 25°. K_1^c and K_2^c represent the primary and the secondary concentration ionisation constant respectively.

trans-Caronic acid.

H_2A × 10^3.	NaOH × 10^3.	*E.M.F.*	$K_1^c \times 10^4$. 25°.	$K_1^c \times 10^4$. 50°.	$K_1^c \times 10^4$. 74°.	NaOH × 10^3.	*E.M.F.*	$K_2^c \times 10^6$. 25°.	$K_2^c \times 10^6$. 50°.	$K_2^c \times 10^6$. 74°.
10·0	5·0	0·6250	1·69	1·47	1·19	15·0	0·7064	8·15	6·33	4·83
5·0	2·5	0·6259	1·72	1·38	1·10	7·5	0·7092	7·25	5·43	4·21
2·5	1·25	0·6288	1·76	1·35	1·08	3·75	0·71296	6·25	4·92	3·73
1·25	0·625	0·6327	1·67	1·32	1·07	1·875	0·7147	5·81	4·50	3·55

Results obtained for the various thermodynamic ionisation constants are recorded below the mean deviations from the mean values approximating to 1% :

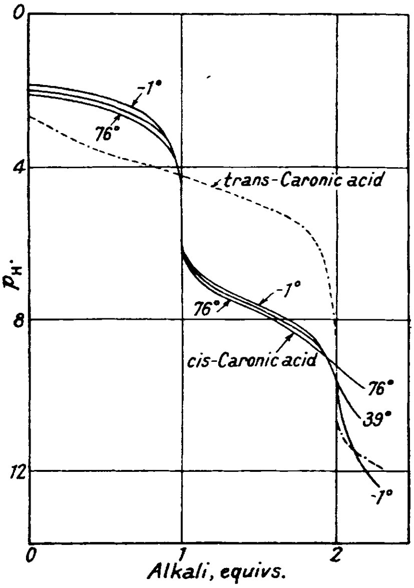
Temp.	$10^5K_1^a$.	$10^8K_2^a$.	K_1^a/K_2^a.	*r*, Å.	Change in *r*, %, for 25—74°.	$10^5K_1^a$.	$10^8K_2^a$.	K_1^a/K_2^a.	*r*, Å.	Change in *r*, %, for 25—74°
	cis-Caronic acid.					ββ-Dimethylglutaric acid.				
25°	459	0·494	931,000	2·59	—	20·1	45·7	440	3·55	—
50	380	0·446	852,000	—	—	1·28	32·6	393	—	—
74	283	0·381	743,000	—	—	9·33	25·2	370	—	—
	*cyclo*Hexane-1 : 1-diacetic acid.					*trans*-Caronic acid.				
25	32·5	10·85	2995	3·18	—	15·2	478	31·8	4·85	—
50	24·25	9·09	2668	—	—	12·1	358	33·8	4·78	2·9
74	17·9	7·80	2295	—	—	10·3	264	39·0	4·71	—
	Succinic acid.					Glutaric acid.				
25	6·89	247	28·0	4·98	—	4·58	389	11·78	7·18	—
50	7·33	230	31·9	4·90	4·0	4·41	343	12·85	6·98	6·8
74	7·37	188	39·2	4·78	—	3·69	247	14·94	6·69	—
	β-Methylglutaric acid.					β-*iso*Propylglutaric acid.				
25	5·61	391	14·35	6·38	—	5·05	308	16·40	5·95	—
50	5·17	318	16·26	6·11	7·8	4·63	237	19·51	5·64	8·6
74	4·29	223	19·24	5·88	—	3·87	167	23·17	5·44	—
	Adipic acid.					*r*-βγ-Diphenyladipic acid.				
25	3·70	386	9·58	8·51	—	6·04	639	9·47	8·69	—
50	3·29	322	10·22	8·38	4·7	5·31	467	11·37	7·64	16·0
74	2·90	255	11·40	8·11	—	3·97	305	13·03	7·30	—

The *trans-dl*-caronic acid, m. p. 212°, and the *cis*-caronic acid, m. p. 178°, were kindly presented by Professor J. L. Simonsen, F.R.S., as was also the anhydride of β-*iso*propylglutaric acid from which the acid, m. p. 102°, was prepared. The diphenyladipic acid was kindly presented by Dr. G. R. Ramage. β-Methylglutaric acid (m. p. 88°), ββ-dimethylglutaric acid (m. p. 102°), and *cyclo*hexane-1 : 1-diacetic acid (m. p. 181°) were prepared by standard methods. Succinic, glutaric, and adipic acids were commercial products thrice recrystallised from conductivity water.

DISCUSSION.

According to Baeyer (*Ber.*, 1896, **29**, 2797), *cis*-caronic acid titrates sharply monobasic at room temperature (indicator not specified), whilst at — 2° it titrates as a dibasic acid. The electrometric titration of this acid was suggested by Professor J. L. Simonsen, and the results are in Fig. 1, which compares the *cis*- and the *trans*-acid and shows the effect of temperature on the p_H changes during neutralisation of the former. The curves were shown to be reversible by back titration with acid. No marked displacement of the curve of the *cis*-acid occurs with change of temperature, and with phenolphthalein no indication of monobasicity is obtained at room temperature. With an indicator of lower p_H range the acid would titrate sharply monobasic, but it is unlikely that Baeyer used such an indicator in view of his reference to Bredt's work on camphoronic acid (*Annalen*, 1896, **292**, 83), in which phenolphthalein was employed. The effect of temperature on the inflexion point at the second neutralisation stage is marked. The second ionisation constant of the *cis*-acid is $0{\cdot}49 \times 10^{-8}$, and the disappearance of the inflexion is due to increased hydrolysis of the salt attendant on the 200% increase of K_w over the temperature range 0—70°. To secure a sharp end-point in the titration of such weak acids, titration should be made at low temperatures.

FIG. 1.

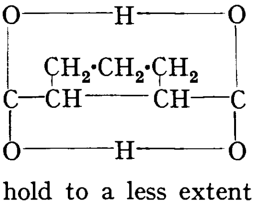


For a constant value of r, the ratio K_1/K_2 should increase with temperature. This increase is observed for all the acids studied, except those having *cis*-structures. That K_1/K_2 decreases with temperature for *cis*-caronic, ββ-dimethylglutaric, and *cyclo*hexane-1 : 1-diacetic acids may indicate that r is increasing with temperature, but an alternative view is that single co-ordination occurs between the carboxyl groups. Such co-ordination of one carbonyl oxygen, causing electron-recession from the hydroxyl oxygen in the same carboxyl group, facilitates ionisation and gives an enhanced value of K_1. The marked decrease in the primary ionisation constants of these *cis*-acids with increase of temperature ($K_1^{25°}$ is approximately twice $K_1^{74°}$) is in harmony with this view, the co-ordination diminishing.

The primary ionisation constants of caronic acid are here compared with those of *cyclo*propane-1 : 2-dicarboxylic acid and its two higher homologues :

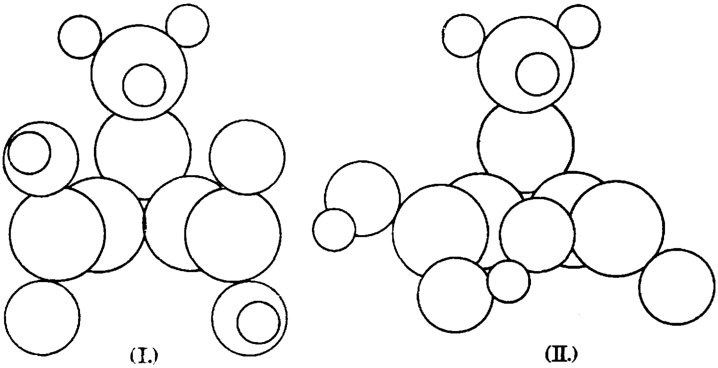
Acid.	$K_1 \times 10^5$. *cis*.	*trans*.	References.
Caronic	459	15·2	
*cyclo*Propane-1 : 2-dicarboxylic	46·8	22·4	Wassermann, *Helv. Chim. Acta*, 1930, **13**, 223.
*cyclo*Butane-1 : 2-dicarboxylic	12·6	16·2	Bode, *Ber.*, 1934, **67**, 332.
	6·3	17·0	Kuhn and Wassermann, *Helv. Chim. Acta*, 1928, **11**, 600.
*cyclo*Pentane-1 : 2-dicarboxylic	3·7	11·0	Ingold and Mohrhenn, J., 1935, 949.

The large value for the primary ionisation constant of *cis*-caronic acid cannot be attributed to the *gem*-dimethyl grouping, for the constant of the *trans*-acid is similar in magnitude to that of *trans-cyclo*propane-1 : 2-dicarboxylic acid. The fact that K_1 for the *cis-cyclo*-pentane- and -*cyclo*butane-1 : 2-dicarboxylic acids is, in each case, less than K_1 for the corresponding *trans*-acids, in spite of the greater proximity of the carboxyl groups, may possibly be due to a double co-ordination of the hydrogens of the carboxyl groups with the carbonyl oxygens of the opposite carboxyl group (see inset). For the pentane acid the distance between the centres of the oxygen atoms of the two carboxyl groups when these are mutually symmetrical is 3·04 Å., or, if the radius of an oxygen atom is taken as 0·60 Å., the net distance between the oxygen atoms is 1·84 Å. The same type of co-ordination may hold to a less extent for *cis-cyclo*butane-1 : 2-dicarboxylic acid. The ratio K_1^{cis}/K_1^{trans} is larger for the butane than for the pentane acids. Calculation, using the valency deflexion theory, shows that the net distance between the oxygen atoms in the undistorted molecule has increased to 2·07 Å. In *cis-cyclo*propane-1 : 2-dicarboxylic acid, the net distance between the oxygen atoms of the two groups has further increased to 2·35 Å., *i.e.*, 0·51 Å. greater than for the *cis-cyclo*pentane acid, and here K_1^{cis} is greater than K_1^{trans}, indicating that such double co-ordination may not now be possible. In *cis*-caronic acid, interference between the *gem*-dimethyl group and the carboxyl groups renders the symmetrical position (I) (Fig. 2) unlikely and favours position (II). If single co-ordination occurs to an appreciable extent, and the model shows that no strain would be involved, augmentation of K_1 would result.



The value of r calculated for *trans*-caronic acid is approximately the same as that for succinic acid, confirming the extended structure for succinic acid. The percentage decrease in *r* over the temperature range 25—74° is slightly less for *trans*-caronic than for succinic acid, though both appear to be rigid. The substitution of a β-methyl group decreases *r* from 7·18 to 6·38 Å. (cf. Ingold and Mohrhenn, *loc. cit.*), and substitution of a β-*iso*propyl group changes it to 5·95 Å. The structure of glutaric acid is still extended, even when the bulky *iso*propyl group is present, until two β-substituents have been introduced. This change in configuration, associated with the introduction of a second β-substituent, may be connected with the parachors of the methyl esters of the glutaric acids (Vogel, J., 1934, 1758) : for the esters of the unsubstituted, the methyl, and the dimethyl acid the parachors are 361·4, 399·9, and 431·8 respectively; the first increment (38·5) is nearly normal for a CH_2 group (39·0), but the second (31·9) is only explicable if the effective volume of the molecule has been diminished by a change in configuration.

FIG. 2.


(I.) (II.)

The lengthening of the hydrocarbon chain from succinic to glutaric acid appears to be attended by an increase in thermal pliability, the percentage decrease in *r* over the temperature range 25—74° being 4·0% for succinic and 6·8% for glutaric acid. For adipic acid the corresponding value is 4·7%. This may possibly be connected with the fact that for the extended chains there is an alternating effect in the orientation and therefore in the mutual repulsion of the terminal carboxyl groups, which would lead to a greater rigidity of the even members of the series. The greater pliability of adipic acid when loaded with two phenyl groups is marked, the decrease in *r* over the same range being 16·0%. This pliability of the molecule is in harmony with the known formation of chrysene derivatives on ring closure (Ramage and Robinson, J., 1933, 607).

The authors thank Professor J. L. Simonsen, F.R.S., for his helpful interest in this work, and the Chemical Society for a grant.

UNIVERSITY COLLEGE OF N. WALES, BANGOR. [*Received, November* 15*th*, 1935.]