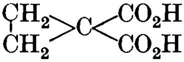
CXCII.—*The Dissociation Constants of Organic Acids. Part II. The Primary Dissociation Constants of Some Cyclic* 1 : 1-*Dicarboxylic Acids.*

By Arthur Israel Vogel.

The *cyclo*propane, *cyclo*butane, *cyclo*pentane, and *cyclo*hexane rings may be regarded as derived from the corresponding open-chain *gem*-dimethyl-, methylethyl-, diethyl- and ethyl-*n*-propyl compounds by the elimination of two hydrogen atoms from, and subsequent ring-closure at, the terminal carbon atoms. The comparison, by means of a trustworthy physicochemical method, of the properties of these two parallel series of compounds will eventually furnish valuable evidence *inter alia* as to the nature of ring closure, the "tetrahedral angle" and the configuration of the rings. In the present paper the cyclic 1 : 1-dicarboxylic acids (I), (II), (III), and (IV) have been investigated by the conductivity method and the results are compared with those obtained for the corresponding open-chain compounds (V), (VI), (VII), and (VIII) described in Part I (preceding paper). No accurate conductivity measurements on cyclic 1 : 1-dicarboxylic acids have previously been made; some old measurements for *cyclo*propane-1 : 1-dicarboxylic acid (Bone and Sprankling, J., 1898, **83**, 1379; Smith, *Z. physikal. Chem.*, 1898, **25**, 204) and for *cyclo*butane-1 : 1-dicarboxylic acid (Stohmann and Kleber, *J. pr. Chem.*, 1892, **45**, 480; Walker, J., 1892, **61**, 705; Smith, *loc. cit.*) are on record.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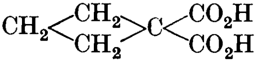
(I.)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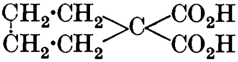
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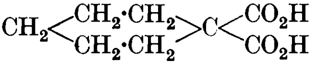
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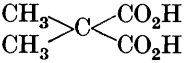
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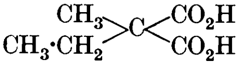
(V.)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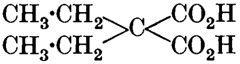
(VI.)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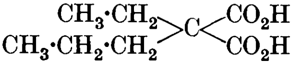
(VII.)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(VIII.)

EXPERIMENTAL.

Preparation and Purification of Acids.—cyclo*Propane*-1 : 1-*dicarboxylic acid.* Pure redistilled ethylene dibromide was condensed with ethyl sodiocyanoacetate (prepared with absolute alcohol distilled over calcium) according to Perkin and Carpenter (J., 1899, **75**, 921), and the ethyl 1-cyano*cyclo*propane-1-carboxylate, b. p. 215—216°/761 mm., hydrolysed by heating on the steam-bath with 6 mols. of ethyl-alcoholic potassium hydroxide for 28 hours. The acid was isolated by ether extraction (three times) after previous saturation with ammonium sulphate, and solidified almost completely when left over calcium chloride in a vacuum desiccator for several hours. The oily matter was absorbed in porous plate, and the acid recrystallised from benzene–ether–light petroleum (b. p. 60—80°); m. p. 110—120°. It was then triturated twice with boiling benzene (to remove malonic acid), but it still melted at 110—125°. Recrystallisation from chloroform raised the m. p. to 132° (softening at 120°), which was unaffected by recrystallisation from other solvents. The acid was then esterified with ethyl alcohol–benzene–sulphuric acid (Vogel, J., 1928, 2020), and the fraction, b. p. 215—216°/759 mm., which was pure ethyl *cyclo*propane-1 : 1-dicarboxylate, hydrolysed by heating under reflux on the steam-bath for 10 hours with 4 mols. of ethyl-alcoholic potassium hydroxide; the acid, isolated by ether extraction, after one crystallisation from benzene–ether–light petroleum (b. p. 40—60°), formed magnificent thin plates, which melted sharply at 136° (Perkin and Carpenter, *loc. cit.*, give m. p. 133—136°; Jones and Scott, *J. Amer. Chem. Soc.*, 1922, **44**, 413, give m. p. 134°). $M = 130{\cdot}05$.

cyclo*Butane*-1 : 1-*dicarboxylic acid.* $\alpha\gamma$-Dibromopropane (Roger Adams, "Organic Syntheses," 1921, **1**, 8) was condensed with ethyl sodiomalonate according to Perkin and Prentice (J., 1891, **59**, 823; compare J., 1887, **41**, 20), and the product distilled in steam. The distillate was saturated with ammonium sulphate and twice extracted with ether. The extract was dried, the ether evaporated, and the residue distilled. The fraction, b. p. 100—116°/14 mm., consisting largely of ethyl *cyclo*butane-1 : 1-dicarboxylate, was hydrolysed by heating on the steam-bath with 4 mols. of ethyl-alcoholic potassium hydroxide for 5 hours; the acid, isolated by five extractions with ether, was spread on a porous plate to remove a small quantity of oily matter. A small proportion of malonic acid present was removed by two triturations with relatively small quantities of boiling benzene, in which malonic acid is readily and the cyclic acid sparingly soluble; the residue, m. p. 157—158° (decomp.), after recrystallisation from benzene–ether, preferably mixed with light petroleum (b. p. 40—60°), formed magnificent thin prisms of the pure acid, m. p. 159° (decomp.) [Perkin and Prentice, *loc. cit.*, give m. p. 154—156° (decomp.); Perkin and Carpenter, *loc. cit.*, give m. p. 157° (decomp.)]. $M = 144{\cdot}06$.

cyclo*Pentane*-1 : 1-*dicarboxylic acid* was prepared by the condensation of $\alpha\delta$-dibromobutane with ethyl sodiomalonate. The most convenient method of preparing $\alpha\delta$-dibromobutane is the following modification of von Braun and Lemke's method (*Ber.*, 1922, **55**, 3526). Adipic acid was converted by means of thionyl chloride into the acid chloride, and the latter into the diamide by aqueous ammonia (*d* 0·88). 214 G. of the crude *finely powdered* diamide were frequently shaken during 30 minutes with a solution prepared from 1480 g. of 33% sodium hydroxide solution (493·5 g. of sodium hydroxide and 986·5 g. of water), 471 g. of bromine, and 1750 g. of ice and the whole was then heated under reflux on the steam-bath for 2 hours; an odour reminiscent of piperidine was soon perceptible. After 12 hours, 437 g. of benzoyl chloride were added with cooling and the mixture was maintained for 18 hours at 30—40° (yield of *NN'*-dibenzoylputrescine, 390 g. after drying in the steam-oven). To 180 g. of the crude dibenzoylputrescine and 323 g. of phosphorus tribromide (2 mols.), 96 g. of bromine (2 mols.) were slowly added. The mixture was melted by gentle heating and slowly distilled under atmospheric pressure, a little hydrogen bromide and phosphorus pentabromide being evolved; when a few c.c. had passed over, the distillation was continued under diminished pressure (water-pump) during $1\frac{1}{2}$—2 hours, the temperature not rising above 120°. The distillate, consisting of phosphorus oxybromide, benzonitrile and αδ-dibromobutane, was poured into ice and water, and the residual heavy oil was extracted in light petroleum (b. p. 40—60°), treated with small quantities of concentrated sulphuric acid until the latter was no longer coloured (three extractions are usually sufficient), in order to remove the benzonitrile, washed with water, dried with calcium chloride, and distilled after evaporation of the solvent, αδ-dibromobutane (62 g.) being obtained as a colourless liquid, b. p. 76—77°/18 mm. (Müller and Sauerwald, *Monatsh.*, 1927, **48**, 156, give b. p. 70—72°/8 mm.; von Braun and Lemke, *loc. cit.*, give b. p. 80—82°/14 mm.). A better yield can be obtained from recrystallised *NN'*-dibenzoylputrescine.

Condensation of αδ-dibromobutane with ethyl sodiomalonate. To a cold solution of sodium ethoxide (from 13·1 g. of sodium, and 240 g. of absolute alcohol distilled over calcium), access of moisture being prevented, ethyl malonate (45·7 g.) was added, followed after 30 minutes by 56·7 g. of the dibromide. The solution, which became neutral when warmed on the steam-bath, was acidified with dilute hydrochloric acid, diluted with water, saturated with ammonium sulphate, and extracted three times with ether. The ethereal solution was washed three times with water and dried with calcium chloride, the ether removed, and the residue distilled under diminished pressure. The fraction, b. p. 100—120°/16 mm. (chiefly at 115°/16 mm.) (30 g.), consisting chiefly of ethyl *cyclo*pentane-1 : 1-dicarboxylate, was heated under reflux with ethyl-alcoholic potassium hydroxide (30 g. of potassium hydroxide in 60 g. of water; 30 g. of ester in 60 g. of rectified spirit) on the steam-bath for 12 hours. The solution was evaporated to dryness, and the residue triturated with ether to remove neutral impurities (if any) and acidified with dilute sulphuric acid. The *cyclo*pentane-1 : 1-dicarboxylic acid, isolated by extraction with ether (four times) in the usual way and drained on porous tile (yield, 18 g.), was triturated three times with boiling benzene to remove the very small quantity of malonic acid present; it then melted at 190° (decomp.) and crystallised from benzene–ether–light petroleum (b. p. 40—60°) in small thin prisms. The acid is very sparingly soluble in boiling benzene and only relatively slightly soluble in cold water and hence it was not possible to extend the conductivity measurements to very concentrated solutions by the method employed in the present research. Stauss (*Ber.*, 1894, **27**, 1229) gives m. p. 176—178° and Haworth and Perkin (J., 1894, **65**, 86) give m. p. 184—185° (decomp.);

the acids obtained by these investigators were probably not pure owing to the use of an impure dibromide in the initial condensation. $M = 158{\cdot}08$.

cyclo*Hexane*-1 : 1-*dicarboxylic acid* (compare Dox and Yoder, *J. Amer. Chem. Soc.*, 1921, **43**, 1366). The reaction between ethyl malonate (91·5 g.), sodium ethoxide (from 26·2 g. of sodium and 480 g. of absolute alcohol), and αε-dibromopentane (b. p. 112—113°/22 mm.; 131·5 g.) was carried out substantially as in the preceding case and after 16 hours' heating on the steam-bath the product was isolated from the neutral solution in the usual way. On distillation, after a small fraction, b. p. 119—130°/16 mm., there was obtained a main fraction, b. p. 130—145°/16 mm. (50 g.). This was heated under reflux for 16 hours with alcoholic potassium hydroxide (50 g. of ester in 100 g. of rectified spirit; 50 g. of potassium hydroxide in 100 g. of water), and the acid isolated as described under *cyclo*pentane-1 : 1-dicarboxylic acid [yield, 36 g.; m. p. 168° (decomp.)]. After two crystallisations from benzene–ether–light petroleum (b. p. 40—60°), from which it separated in small thin prisms, the acid melted at 179·5° (decomp.) [Wightman, J., 1926, 2541, gives m. p. 176° (decomp.); the m. p. 207°, given by Ingold and Thorpe, J., 1919, **115**, 376, requires correction].

Although the condensations of αδ-dibromobutane and of αε-dibromopentane with ethyl sodiomalonate were carried out under comparable conditions, the yield of *cyclo*pentane-1 : 1-dicarboxylic was definitely greater than that of *cyclo*hexane-1 : 1-dicarboxylic acid, thus providing further evidence for the conclusion (this vol., p. 721) that the 5-membered ring is formed more readily than the 6-membered ring.

Owing to the relatively sparing solubility of the acid in water at 25°, the conductivity measurements could not be extended to concentrated solutions. $M = 172{\cdot}10$.

The acids were kept over calcium chloride and paraffin wax in vacuum desiccators until required.

Disodium Salts.—These were prepared by adding the calculated quantity of *N*-sodium hydroxide, 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 ethyl alcohol. All the salts were dried at 120—130° for 6 hours and then stored over calcium chloride in a vacuum desiccator until required for use. The molecular weights employed for the disodium salts were *cyclo*propane- 174·03, *cyclo*butane- 188·05, *cyclo*pentane- 202·06, and *cyclo*hexane-1 : 1-dicarboxylate 216·08.

Conductivity Measurements.—The technique of the conductivity measurements was identical with that described in Part I (preceding paper) and the same conductivity cells were employed; the cell constants were redetermined at frequent intervals but no change could be detected. The water used had a specific conductivity of 0·8—0·9 × 10^{-6} mho. All the measurements were carried out at 25° ± 0·01°. It was usual to carry out at least two experiments for each substance.

Results.—Owing to limitations of space the actual experimental results for only one series of measurements for one acid and its disodium salt will be given; these are typical of all the results obtained and are in Table I. The specific conductivity of the solvent is given by κ. Tabulated results for the acids are in Table II, in which are presented the values of the molecular conductivity, μ, at round concentrations, C, above 2 × 10^{-3} molar and the corresponding values of the primary dissociation constant, K_1, together with the values of μ_0, the molecular conductivity at infinite dilution of the acid ionising as a uni-univalent electrolyte, computed in the

TABLE I.

Cell constant, 0·022996.

*cyclo*Butane-1 : 1-dicarboxylic acid.	$C \times 10^4$.	μ.	Disodium *cyclo*butane-1 : 1-dicarboxylate.	$C \times 10^4$.	μ.
Series (b)	1·1509	330·6	Series (b)	1·8062	197·2
$\kappa \times 10^7$, 9·240	3·4957	280·3	$\kappa \times 10^7$, 9·537	3·0270	196·3
	9·1826	221·6		6·3168	194·4
	15·958	186·3		11·158	191·7
	27·129	154·9		17·271	189·0
	39·090	135·1		24·373	186·5
	51·695	121·2		32·850	184·1
	74·381	104·6		46·716	181·3
	94·843	94·6			

TABLE II.

	*cyclo*Propane-1 : 1-dicarboxylic acid.		*cyclo*Butane-1 : 1-dicarboxylic acid.		*cyclo*Pentane-1 : 1-dicarboxylic acid.		*cyclo*Hexane-1 : 1-dicarboxylic acid.	
	μ_0 = 402·45.		μ_0 = 397·0.		μ_0 = 395·95.		μ_0 = 394·2.	
$C \times 10^3$.	μ.	$K_1 \times 10^4$.	μ.	$K_1 \times 10^4$.	μ.	$K_1 \times 10^1$.	μ.	$K_1 \times 10^4$.
2	333·6	80·3	172·6	6·69	156·9	5·20	128·0	3·12
3	320·8	94·0	148·7	6·73	136·4	5·43	108·6	3·14
4	309·9	103·1	134·1	6·89	122·1	5·50	96·2	3·15
5	300·3	109·7	123·1	6·97	111·0	5·46	88·3	3·16
6	292·0	115·1	114·2	6·97	102·0	5·49	83·1	*3·38
7	284·8	119·9	107·0	6·96	$K_1 = 5·47 \times 10^{-4}$.		$K_1 = 3·14 \times 10^{-4}$.	
8	278·3	124·0	101·0	6·95				
9	272·8	131·4	96·2	6·97				
	K_1 = *ca.* 1·4 × 10^{-2} (?).		$K_1 = 6·96 \times 10^{-4}$.					

* Not employed in calculation of mean.

manner described in the first paper of this series. Table III contains the results for the acids at concentrations below 2×10^{-3} molar. The values of μ have been interpolated from a large-scale conductivity–concentration curve; a smooth curve could always be drawn without ambiguity through the experimental results. The values of the molecular conductivity of the disodium salts over a range of concentration are incorporated in Table IV; μ_0, the molecular conductivity at infinite dilution, has been calculated by means of the equation $\mu_0 = \mu + bC^n$ by the graphical method of Ferguson and Vogel (*Phil. Mag.*, 1925, **50**, 971).

TABLE III.

	*cyclo*Propane-1 : 1-dicarboxylic acid.		*cyclo*Butane-1 : 1-dicarboxylic acid.		*cyclo*Pentane-1 : 1-dicarboxylic acid.		*cyclo*Hexane-1 : 1-dicarboxylic acid.	
$C \times 10^4$.	μ.	$K_1 \times 10^4$.	μ.	$K_1 \times 10^4$.	μ.	$K_1 \times 10^4$.	μ.	$K_1 \times 10^4$.
1	365·0	8·8	333·1	4·37	—	—	—	—
2	363·0	16·6	305·8	5·17	282·7	3·56	259·5	2·54
5	357·3	35·1	259·1	6·13	232·9	4·20	205·1	2·82
10	348·8	56·4	217·1	6·60	196·0	4·85	165·6	3·04

TABLE IV.

Disodium 1 : 1-dicarboxylates.

	*cyclo*Propane-.	*cyclo*Butane-.	*cyclo*Pentane-.	*cyclo*Hexane-.
$C \times 10^4$.	μ.	μ.	μ.	μ.
2	207·3	197·1	194·9	190·9
5	204·9	195·1	193·0	188·8
10	201·6	192·4	190·3	186·0
20	196·7	188·0	186·2	182·0
30	193·0	184·9	183·1	179·1
35	191·4	183·6	181·8	178·0
40	190·1	—	—	—
μ_0	209·6	198·75	196·65	193·1

A conspectus of the results is exhibited in Tables V and VI; $l_{X^{--}}$ is the ionic conductivity at infinite dilution of the neutral anion deduced from measurements on the disodium salts, and b and n are the constants used in the computation of μ_0 for the disodium salts.

TABLE V.

Acid.	μ_0.	K_1.
(A) *cyclo*Propane-1 : 1-dicarboxylic acid	402·45	*ca.* $1·4 \times 10^{-3}$
(B) *cyclo*Butane-1 : 1-dicarboxylic acid	397·0	$6·96 \times 10^{-4}$
(C) *cyclo*Pentane-1 : 1-dicarboxylic acid	395·95	$5·47 \times 10^{-4}$
(D) *cyclo*Hexane-1 : 1-dicarboxylic acid	394·2	$3·14 \times 10^{-4}$

TABLE VI.

Disodium salt of	μ_0.	$l_{X^{--}}$.	b.	n.
A	209·6	106·8	1105	0·7151
B	198·75	95·95	1498	0·7924
C	196·65	93·8	1127	0·7521
D	193·1	90·3	805	0·6870

Discussion.—Inspection of the Tables reveals the following results. *cyclo*Propane-1 : 1-dicarboxylic acid is a very strong acid, but it does not give a constant value for K_1 over the whole of the concentration range studied; it simulates di-*n*-propylmalonic acid (Vogel, this vol., p. 1486) in this respect. *cyclo*Butane-, *cyclo*pentane- and *cyclo*hexane-1 : 1-dicarboxylic acids are relatively weak acids and ionise as uni-univalent electrolytes according to the simple mass-action law over a definite concentration range; moreover, the variation of the dissociation constant over the whole range of concentration is relatively small, but the diminution of K_1 at low concentrations is quite definite (Table III). For these three acids the values of the primary dissociation constants, the conductivity at infinite dilution of the disodium salts and hence the mobilities of the anions, $l_{X^{--}}$, and the values of b and n in the equation $\mu_0 = \mu + bC^n$ *decrease* regularly with increase in the size of the ring. There seems at present no apparent connexion between the primary dissociation constants of the *cyclo*propane-, *cyclo*butane-, *cyclo*pentane- and *cyclo*hexane-1 : 1-dicarboxylic acids and those of the *gem*-dimethyl- ($6{\cdot}57 \times 10^{-4}$), methylethyl- ($13{\cdot}94 \times 10^{-4}$), diethyl- ($63{\cdot}9 \times 10^{-4}$) and ethyl-*n*-propyl- ($73{\cdot}7 \times 10^{-4}$) malonic acids, the open-chain compounds from which they may be regarded as derived.

A full discussion of the significance of these results is reserved pending the completion of the work in progress on the determination (if possible) of the so-called secondary ionisation constants of these acids together with the investigation, on the lines described in Part I, of some monocyclylmalonic acids (*e.g.*, *cyclo*pentyl, *cyclo*hexyl, *cyclo*heptyl, etc.), of the normal dibasic acids (succinic acid and higher members), and of the substituted succinic and glutaric acids. It should, however, be mentioned here that the anomalous character of the *cyclo*propane ring in the 1 : 1-dicarboxylic compounds is also reflected in the chemical properties; *e.g.*, Bone and Perkin (J., 1895, **67**, 112) found that ethyl *cyclo*propane-1 : 1-dicarboxylate reacts with ethyl sodiomalonate with the formation of the open-chain compound ethyl butane-ααδδ-tetracarboxylate (compare Best and Thorpe, J., 1909, **95**, 692; Campbell and Thorpe, J., 1910, **97**, 2418) and Perkin (J., 1885, **47**, 801) showed that the acid is readily decomposed by hydrobromic acid, giving ethyl-bromomalonic acid.

No account has been taken of interionic forces and related effects in the present calculations of the primary dissociation constants (compare Sherrill and Noyes, *J. Amer. Chem. Soc.*, 1926, **48**, 1861; MacInnes, *ibid.*, p. 2068); this question will be considered in a future communication.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
LONDON, S.W. 7.

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