

# DISSOCIATION CONSTANTS OF *CIS* AND *TRANS* CARONIC AND NORPINIC ACIDS.

By C. T. Abichandani and S. K. K. Jatkar.

The potentiometric titrations of *cis* and *trans*-caronic, and norpinic acids have been carried out in order to determine the nature of the pH titration curves and to calculate the primary and secondary dissociation constants. The distance between the two ionising carboxyl groups has been calculated with the help of Bjerrum's (*Z. Physikal Chem.*, 1923, 106, 219) empirical formula.

## EXPERIMENTAL.

The pH measurements were made with a hydrogen electrode in a cell described previously (*This Journal*, 1938, 21A, 345). A saturated calomel half-cell was used as a reference electrode. The electro-motive force measurements were made on a Tinsley's vernier potentiometer using a mirror galvanometer as a null instrument. All the titrations were carried out at room temperature.

Hydrogen prepared by electrolysis of 10% caustic soda solution with nickel electrodes, was purified by passing through a tube containing palladinized asbestos. A stainless steel tube 3 ft. long and one inch in diameter, heated to about 230°, was used for this purpose. Before admitting the gas to the titration vessel, it was passed through water to avoid concentration changes.

All the acids were prepared in the Organic Chemistry Department of the Institute. *Trans*-caronic acid (m.p. 212–13°) was prepared by condensation of dimethyldiazomethane with fumaric or maleic ester (*Ber.*, 1937, 70, 1688). The ester obtained was hydrolysed with alkali, acidified and extracted with ether. *Cis*-caronic acid (m.p. 176°) was obtained by treatment of the *trans*-acid with acetic anhydride in a sealed tube for six hours. The product was distilled and acid separated by crystallization from hot water. *Trans*-norpinic acid (m.p. 146°) was prepared by Kerr's method starting with Guareshi imide and methylene iodide (*Jour. Amer. Chem. Soc.*, 1929, 51, 614). *Cis*-norpinic acid (m.p. 175°) was prepared from *trans*, by the same method as in the case of *cis*-caronic acid.

The solution to be titrated was prepared by dissolving a known weight of the acid in distilled water and diluted to 250 c.c. The two caronic acids dissolved easily in water, while the two norpinic acids went completely in solution only after the addition of about 2 c.c. of 0.1 N alkali.

Standard sodium hydroxide solution was prepared by the action of water vapour on metallic sodium, taking all precautions to exclude carbon dioxide. The solution was stored in a four litre bottle coated inside with paraffin wax and fitted with an outlet tube connected to a burette and an inlet tube containing soda lime.

*Procedure.*—After placing the solution in the titration vessel, hydrogen was bubbled through the electrode system for about two hours till the equilibrium was reached. The electrodes were checked against 0.05 N potassium phthalate buffer, the pH value found being 3.95 which was in good agreement with 3.96 obtained by Burton, Hamer and Acree (*Jour. Bureau of Standards*, 1936, 16, 575). When equilibrium was set up between the electrodes, a certain quantity of standard alkali was added and electromotive force recorded. This procedure was repeated till the end point of titration was reached.

*Determination of pH Value.*—The pH value at any point was computed from the equation 
$$\text{pH} = \frac{E - E_0}{2.3026 \frac{RT}{F}}$$
 where  $E$  is the observed potential of the cell: Pt;  $H_2$ |Solution X|KCl (sat)|reference electrode,  $E_0$  is the potential of saturated calomel electrode and  $R$ ,  $T$  and  $F$  have their usual significance.

The junction potential  $E_L$  between solution X and KCl (sat), being very small, was neglected. Fales and Vosburgh (*Jour. Amer. Chem. Soc.*, 1918, 40, 1291) while studying the applicability of Plank and Hendersen formula for the calculation of  $E_L$  have come to the conclusion that there is no measurable potential difference between saturated solution of potassium chloride and hydrochloric acid solutions ranging from 0.1 N to 1.0 N. Due to the inconvenience of calculation of  $E_L$ , MacInnes, Belcher and Shedlovsky (*Jour. Amer. Chem. Soc.*, 1938, 60, 1094) have incorporated this in the value of  $E_0$  and modified the latter. Taking their values for 0.1 N calomel electrode and for the cell Hg; HgCl|KCl(sat)|KCl (0.1 N), HgCl; Hg, the value of  $E_0$  for saturated calomel at 30° C. is 0.2418 volts, being 0.2 m.v. (.003 pH units) lower than Clark's value (*Determination of Hydrogen Ions*, 3rd Ed., 1928).

The titration data and the dissociation constants are given in the following tables:—

(1) *Cis*-CARONIC ACID.

TABLE I. Stoichiometrical concentrations prevailing in the titration of 250 c.c. of 0.002205 M acid by 0.0718 N sodium hydroxide.

0.0718 N NaOH	Moles NaOH per mole acid	J = equiv. conc. of Na salt $\times 10^{-4}$	$M_{H_2A} \times 10^{-4}$	$M_{HA} = U \times 10^{-4}$	$M_{NaHA} \times 10^{-4}$	$M_{Na_2A} \times 10^{-4}$
0.0	0.0000	0.00	22.05	22.05	0.00	..
1.0	.1302	2.86	21.96	19.10	2.86	..
2.1	.2735	5.98	21.85	15.87	5.98	..
3.0	.3907	8.51	21.78	13.27	8.51	..
3.5	.4559	9.91	21.74	11.83	9.91	..
4.0	.5210	11.30	21.70	10.40	11.30	..
4.5	.5861	12.69	21.65	8.96	12.69	..
5.0	.6512	14.12	21.60	7.48	14.12	..
5.5	.7164	15.45	21.56	6.11	15.45	..
6.0	.7814	16.82	21.52	4.70	16.82	..
7.0	.9117	19.59	21.43	1.84	19.59	..
7.5	.9769	20.91	21.39	0.48	20.91	..
8.0	1.0420	22.25	21.34	..	20.43	0.91
9.0	1.1735	24.95	21.26	..	17.57	3.69
10.0	1.3024	27.55	21.17	..	14.79	6.38
10.5	1.3676	28.94	21.13	..	13.32	7.81
11.0	1.4327	30.40	21.10	..	11.80	9.30
11.5	1.4979	31.57	21.07	..	10.57	10.50
12.0	1.5628	32.90	21.04	..	9.18	11.86
12.5	1.6281	34.19	21.00	..	7.81	13.19
13.0	1.6930	35.49	20.97	..	6.45	14.52
13.5	1.7583	36.79	20.94	..	5.09	15.85
14.0	1.8234	38.04	20.90	..	3.76	17.14
15.0	1.9506	40.64	20.79	..	0.84	19.85
15.4	2.0058	41.66	20.75	..	..	20.91

TABLE II. Data for the Titration of 0.002205 M *cis*-Caronic Acid at 26.8° C. First Equivalent of Sodium Hydroxide

Calomel temp.	0.0718 N NaOH	E.M.F.	pH	$C_H \times 10^2$	$n$	$K_1^c \times 10^{-4}$	$\mu \times 10^{-4}$	$K_1^a \times 10^{-4}$
26.5	0.0	0.4351	3.21	6.166	4	..	..	..
26.6	1.0	.4422	3.32	4.788	4	2.57	7.64	2.49
26.8	2.1	.4511	3.48	3.311	4	2.46	9.31	2.38
27.1	3.0	.4591	3.61	2.455	4	2.49	10.96	2.40
27.3	3.5	.4638	3.69	2.042	4	2.50	11.95	2.40
..	4.0	.4683	3.77	1.698	4	2.54	13.00	2.44
..	4.5	.4747	3.87	1.349	4	2.57	14.04	2.46
27.5	5.0	.4808	3.98	1.047	4	2.47	15.17	2.37
..	5.5	.4862	4.08	8.313	5	2.56	16.28	2.45
27.8	6.0	.4918	4.17	6.761	5	2.94	17.50	..
..	7.0	.5028	4.36	4.365	5	6.32	20.03	..

## Second Equivalent of Sodium Hydroxide.

						$K_2^c \times 10^{-6}$	$K_2^a \times 10^{-6}$
27.8	8.0	.5135	4.54	2.884	5	1.17	23.74
..	9.0	.5245	4.72	1.905	5	4.37	29.03
..	10.0	.5345	4.89	1.288	5	5.71	34.18
..	10.5	.5412	5.01	9.772	6	5.84	36.95
27.9	11.0	.5486	5.13	7.413	6	5.91	39.94
..	11.5	.5542	5.23	5.888	6	5.91	42.19
..	12.0	.5602	5.33	4.677	6	6.10	44.86
..	12.5	.5671	5.44	3.631	6	6.18	47.46
..	13.0	.5744	5.57	2.692	6	6.10	50.07
28.0	13.5	.5881	5.73	1.826	6	5.72	52.68
..	14.0	.5961	5.93	1.175	6	5.38	55.20
..	15.0	.6377	6.57	2.692	7	6.36	60.49
..	15.4	.7525	8.49	3.236	9	..	..

$$K_1^a = 2.42 \times 10^{-4}$$

$$K_2^a = 4.76 \times 10^{-6}$$

(2) *Trans*-CARONIC ACID.

TABLE I. Stoichiometrical concentrations prevailing in the titration of 250 c.c. of 0.003455 M acid by 0.0718 N sodium hydroxide.

0.0718 N NaOH	Moles NaOH per mole acid	J = equiv. conc. of Na salts $\times 10^{-4}$	$M_{H_2A_n} \times 10^{-4}$	$M_{HA_n} = U \times 10^{-4}$	$M_{NaHA_n} \times 10^{-4}$	$M_{Na_2A_n} \times 10^{-4}$
0.0	0.0000	0.0	34.55	34.55	0.0	..
1.6	.1330	4.57	34.36	29.79	4.57	..
3.03	.2519	8.60	34.14	25.54	8.60	..
4.0	.3325	11.30	34.00	22.70	11.30	..
5.01	.4165	14.12	33.88	19.70	14.12	..
7.02	.5835	19.60	33.61	14.01	19.60	..
8.0	.6650	22.25	33.50	11.25	22.25	..
9.0	.7481	24.95	33.37	8.42	24.95	..
10.05	.8354	27.60	33.26	5.66	27.60	..
11.0	.9143	30.40	33.11	2.71	30.40	..
12.0	.9975	32.90	32.98	0.80	32.90	..
13.0	1.0806	35.49	32.82	..	30.15	2.67
14.0	1.1637	38.04	32.70	..	27.36	5.34
15.0	1.2468	40.64	32.59	..	24.54	8.05
16.0	1.3299	43.20	32.47	..	21.74	10.73
17.0	1.4120	45.75	32.35	..	18.95	13.40
18.0	1.4691	48.20	32.21	..	16.22	15.99
19.0	1.5792	50.72	32.08	..	13.44	18.64
21.12	1.7536	55.98	31.84	..	7.70	24.14
22.0	1.8288	58.10	31.74	..	5.38	26.36
23.0	1.9119	60.41	31.63	..	2.85	28.78
24.0	1.9950	62.88	31.52	..	0.16	31.36

TABLE II. Data for the Titration of 0.003455 M *trans*-Caronic Acid at 27° C. First Equivalent of Sodium Hydroxide.

Calomel temp.	0.0718 N NaOH	E.M.F.	pH	$C_R \times 10^{12}$	$n$	$K_1^c \times 10^{-4}$	$\mu \times 10^{-4}$	$K_1^a \times 10^{-4}$
26.9	0.0	0.4302	3.13	7.413	4	..	..	..
27.1	1.6	.4366	3.23	5.888	4	2.58	10.46	2.49
27.3	3.03	.4457	3.38	4.169	4	2.49	12.77	2.39
..	4.0	.4511	3.47	3.388	4	2.58	14.69	2.47
27.4	5.01	.4561	3.56	2.754	4	2.74	16.87	2.62
..	7.02	.4709	3.81	1.549	4	2.63	21.15	2.50
..	8.0	.4781	3.93	1.175	4	2.71	23.42	2.57
..	9.0	.4875	4.09	8.125	5	2.75	25.76	2.60
27.8	10.05	.4934	4.20	6.310	5	3.54	28.23	..
..	11.0	.5020	4.34	4.571	5	4.84	30.80	..

## Second Equivalent of Sodium Hydroxide.

					$K_2^c \times 10^{-6}$	$K_2^a \times 10^{-6}$		
28.0	13.0	.5144	4.52	3.020	5	3.01	38.76	..
..	14.0	.5199	4.69	2.042	5	4.16	43.78	..
..	15.0	.5290	4.80	1.585	5	5.34	49.00	..
..	16.0	.5359	4.92	1.202	5	6.03	54.17	..
..	17.0	.5405	5.00	1.000	5	7.16	59.35	5.59
..	18.0	.5480	5.13	7.413	6	7.39	64.33	5.71
..	19.0	.5571	5.28	5.248	6	7.33	69.46	5.61
..	21.12	.5781	5.63	2.344	6	7.38	80.16	5.65
..	22.0	.5897	5.82	1.514	6	7.45	84.49	5.66
28.1	23.0	.6041	6.05	8.913	7	9.04	89.21	..
..	24.0	.6578	6.96	1.096	7	..	94.24	..

$$K_1^a = 2.52 \times 10^{-4}$$

$$K_2^a = 5.60 \times 10^{-6}$$

(3) *Cis*-NORPINIC ACID.

TABLE I. Stoichiometrical concentrations prevailing in the titration of 250 c.c. of 0.008167 M acid by 0.089 N sodium hydroxide.

0.089 N NaOH	Moles NaOH per mole acid	J = equiv. conc. of Na salts $\times 10^{-4}$	$M_{H_2A} \times 10^{-4}$	$M_{HA} = U \times 10^{-4}$	$M_{NaHA} \times 10^{-4}$	$M_{Na_2A} \times 10^{-4}$
0.0	0.0000	0.00	31.67	31.67	0.00	..
1.0	.1124	3.54	31.54	28.00	3.54	..
2.0	.2248	7.06	31.42	24.36	7.06	..
3.0	.3372	10.16	31.29	21.13	10.16	..
4.0	.4496	14.03	31.16	17.13	14.03	..
5.0	.5620	17.45	31.04	13.59	17.45	..
6.0	.6744	20.85	30.91	10.06	20.85	..
7.0	.7868	24.25	30.78	6.53	24.25	..
8.0	.8992	27.60	30.66	3.06	27.60	..
8.5	.9555	29.26	30.59	1.33	29.26	..
9.0	1.0116	30.90	30.53	..	30.16	0.37
10.0	1.1241	34.22	30.40	..	26.58	3.82
11.0	1.2365	37.50	30.28	..	23.06	7.22
12.0	1.3489	40.73	30.18	..	19.63	10.55
13.0	1.4613	44.03	30.09	..	16.15	13.94
14.0	1.5737	47.20	29.99	..	12.78	17.21
15.0	1.6861	50.40	29.86	..	9.32	20.54
16.0	1.7985	53.50	29.74	..	5.93	23.76
17.0	1.9009	56.70	29.64	..	2.58	27.06
17.8	2.0009	59.16	29.55	..	..	29.61

TABLE II. Data for the Titration of 0.008167 M *cis*-Norpinic Acid at 21.8° C. First Equivalent of Sodium Hydroxide.

Calomel temp.	0.089 N NaOH	E.M.F.	pH	$C_H \times 10^{12}$	$\beta$	$K_1^c \times 10^{-4}$	$\mu \times 10^{-4}$	$K_1^a \times 10^{-4}$
21.0	0.0	0.4046	2.88	5.051	3	..	..	..
21.3	1.0	.4261	3.06	9.731	4	..	..	..
21.5	2.0	.4473	3.40	3.981	4	2.16	11.04	..
21.8	3.0	.4609	3.64	2.291	4	1.61	12.45	1.45
22.0	4.0	.4721	3.81	1.549	4	1.55	15.58	1.48
..	5.0	.4826	4.00	1.000	4	1.47	18.45	1.40
22.4	6.0	.4914	4.16	6.981	5	1.61	21.55	1.63
22.6	7.0	.5022	4.35	4.467	5	1.81	24.70	1.71
23.3	8.0	.5112	4.52	3.020	5	3.05	27.90	..
23.5	8.5	.5180	4.64	2.291	5	6.14	29.49	..

## Second Equivalent of Sodium Hydroxide.

					$K_2^c \times 10^{-6}$	$K_2^a \times 10^{-6}$		
23.7	9.0	.5230	4.72	1.905	5	0.37	31.67	..
23.8	10.0	.5306	4.85	1.413	5	2.12	38.82	..
..	11.0	.5361	4.98	1.047	5	3.54	44.92	2.69
..	12.0	.5488	5.17	0.761	6	3.67	51.42	2.81
..	13.0	.5612	5.37	4.266	6	3.70	58.06	2.81
23.9	14.0	.5721	5.55	2.818	6	3.81	64.67	2.95
..	15.0	.5826	5.74	1.820	6	4.02	70.98	3.05
..	16.0	.5959	5.97	1.072	6	4.27	77.28	..
23.8	17.0	.6188	6.35	4.467	7	4.69	83.76	..
24.0	17.5	.6614	..	..	..	..	..	..
..	17.6	.7212	..	..	..	..	..	..
..	17.7	.7977	..	..	..	..	..	..
23.9	17.8	.8180	9.73	1.862	10	..	..	..

$$K_1^a = 1.47 \times 10^{-4}$$

$$K_2^a = 2.84 \times 10^{-6}$$

(4) *Trans*-NORPINIC ACID.

TABLE I. Stoichiometrical concentrations prevailing in the titration of 250 c.c. of 0.002720 M acid by 0.089 N sodium hydroxide.

0.089 N NaOH	Moles NaOH per mole acid	J = equiv. conc. of Na salts $\times 10^{-4}$	$M_{H_2An} \times 10^{-4}$	$M_{H_2An} = U \times 10^{-4}$	$M_{NaHA_n} \times 10^{-4}$	$M_{Na_2A_n} \times 10^{-4}$
0.0	0.0000	0.00	27.20	27.20	0.00	..
1.0	.1309	3.54	27.09	23.55	3.54	..
2.0	.2618	7.06	26.98	19.92	7.06	..
3.0	.3926	10.16	26.87	16.71	10.16	..
3.5	.4581	12.28	26.82	14.54	12.28	..
4.0	.5236	14.03	26.76	12.73	14.03	..
4.5	.5890	15.73	26.71	10.98	15.73	..
5.0	.6544	17.45	26.65	9.20	17.45	..
5.5	.7199	19.15	26.60	7.45	19.15	..
6.0	.7852	20.85	26.55	5.70	20.85	..
6.5	.8507	22.55	26.49	3.94	22.55	..
7.0	.9160	24.25	26.44	2.19	24.25	..
7.5	.9816	25.92	26.38	0.46	25.92	..
8.0	1.0472	27.60	26.33	..	25.06	1.27
9.0	1.1780	30.90	26.22	..	21.54	4.68
10.0	1.3089	34.22	26.14	..	18.06	8.08
10.5	1.3743	35.87	26.08	..	16.37	9.71
11.0	1.4397	37.60	26.03	..	14.56	11.47
11.5	1.5051	39.13	25.97	..	12.81	13.16
12.0	1.5704	40.73	25.92	..	11.11	14.81
12.5	1.6359	42.38	25.87	..	9.36	16.51
13.0	1.7012	44.03	25.84	..	7.65	18.19
13.5	1.7667	45.69	25.79	..	5.99	19.80
14.0	1.8320	47.20	25.76	..	4.32	21.44
15.0	1.9628	50.38	25.68	..	0.98	24.70
15.3	2.0025	51.33	25.62	..	..	25.71

TABLE II. Data for the Titration of 0.002720 M *trans*-Norpinic Acid at 22.6° C. First Equivalent of Sodium Hydroxide.

Calomet temp.	0.089 N NaOH	E.M.F.	pH	$C_N \times 10^{12}$	$n$	$K_1^c \times 10^{-4}$	$\mu \times 10^{-4}$	$K_1^a \times 10^{-4}$
24.0	2.0	0.4407	3.31	4.898	4	3.90	11.96	..
24.1	3.0	.4536	3.51	3.090	4	3.01	13.25	2.89
..	3.5	.4601	3.64	2.291	4	2.73	14.57	2.62
24.0	4.0	.4649	3.73	1.862	4	2.72	15.89	2.60
..	4.5	.4720	3.85	1.413	4	2.53	17.14	2.42
..	5.0	.4764	3.94	1.148	4	2.67	18.60	2.55
24.2	5.5	.4825	4.04	9.120	5	2.80	20.06	2.67
..	6.0	.4895	4.15	7.079	5	3.04	21.56	2.89
..	6.5	.4988	4.28	5.248	5	3.49	23.03	..
24.5	7.0	.5061	4.44	3.631	5	4.80	24.58	..

## Second Equivalent of Sodium Hydroxide.

					$K_2^c \times 10^{-6}$	$K_2^a \times 10^{-6}$		
24.8	8.0	.5182	4.63	2.344	5	1.42	29.33	..
..	9.0	.5244	4.75	1.778	5	4.04	35.94	..
..	10.0	.5335	4.90	1.259	5	5.76	42.55	..
..	10.5	.5378	4.98	1.047	5	6.31	45.78	..
..	11.0	.5419	5.05	8.913	6	7.12	49.15	5.67
..	11.5	.5491	5.17	6.761	6	7.00	52.43	5.54
24.9	12.0	.5552	5.27	5.370	6	7.21	55.64	5.66
..	12.5	.5613	5.38	4.169	6	7.40	58.97	5.77
..	13.0	.5682	5.50	3.169	6	7.55	62.28	5.85
..	13.5	.5762	5.64	2.291	6	7.60	65.43	5.86
24.8	14.0	.5906	5.88	1.318	6	6.56	68.66	..

$$K_1^a = 2.66 \times 10^{-4}$$

$$K_2^a = 5.73 \times 10^{-6}$$

## DISCUSSION.

In Figs. 1 to 4 the titration curves of the various acids are shown along with those indicating the change of mole fraction of the mono-sodium salt formed, with pH. The values of stoichiometrical concentrations of the added alkali, total acid, unneutralized acid, mono-sodium salt and the di-salt, are given in Table I for each acid. The dissociation constants  $K_1^a$  and  $K_2^a$  given in the last column in Table II have been calculated from ionic concentrations and corrected for ionic strength  $\mu$ , according to the method which will be discussed in a later communication. The calculations of  $K_1^a$  and  $K_2^a$  are based on the assumption that each acid group behaves like a monobasic acid and the neutralization of the first and second group proceeds separately. This, however, is not true throughout the whole range of titration, as is evident from the apparent values of  $K_1^a$  and  $K_2^a$  obtained in the middle portion of the titration. It is well known that a dibasic

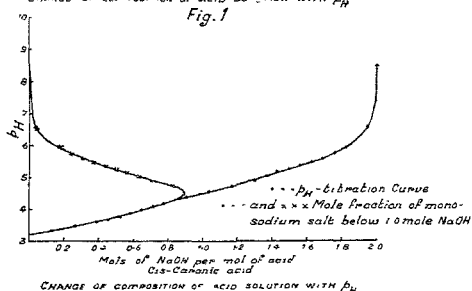
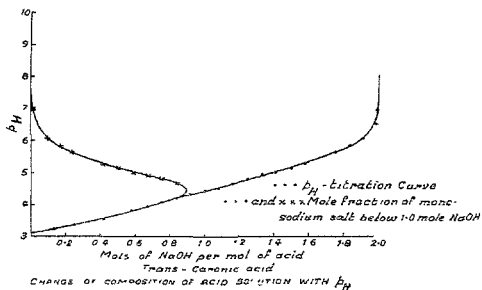
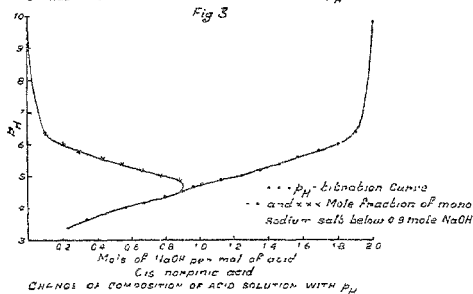
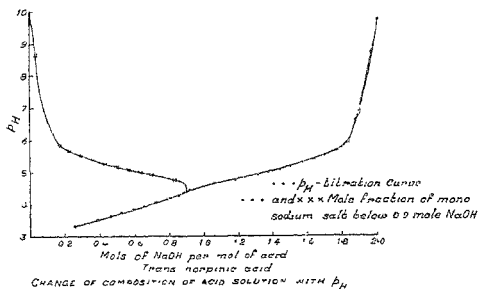


Fig. 2

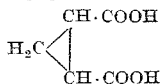


acid may be titrated as a monobasic acid within 1%, if the ratio  $K_1^2/K_2^2$  is 5000. Since in our case the ratio is much smaller, an error approximately of 35% is introduced in this region. It is observed that in the case of *cis* acids, a constant value of  $K_1^2$  is obtained until about 65% of the acid is neutralized, and beyond these limits, the value increases rapidly, indicating the titration of the second group before the first group is completely neutralized. In the second half of the titration, the values of  $K_2^2$  vary, until about 35% of the second group has been neutralized. Thus there is a range of 70%, over which both the acid groups titrate simultaneously. From Figs. 2 and 4 it is seen that the curves for *cis* acids show a slight inflection in the middle, which can be seen more clearly if a differential graph is plotted. This inflection is not so prominent in *trans* acids, in which, the region over which both the groups titrate simultaneously is over 75%.



A comparison of the dissociation constants of caronic and norpinic acids with those of the corresponding cyclo-propane and cyclo-butane dicarboxylic acids obtained by Wasserman (*Helv. Chim. Acta*, 1930, 13, 207, 223) is given below:

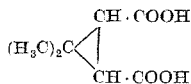
Cyclo-propane 1.2 dicarboxylic acid



$$\text{Cis} \begin{cases} K_1^a = 4.7 \times 10^{-4} \\ K_2^a = 3.4 \times 10^{-7} \\ K_1^a/K_2^a = 138 \end{cases}$$

$$\text{Trans} \begin{cases} K_1^a = 2.2 \times 10^{-4} \\ K_2^a = 7.4 \times 10^{-6} \\ K_1^a/K_2^a = 30 \end{cases}$$

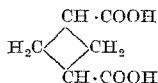
Caronic acid



$$\text{Cis} \begin{cases} K_1^a = 2.42 \times 10^{-4} \\ K_2^a = 4.76 \times 10^{-6} \\ K_1^a/K_2^a = 51 \end{cases}$$

$$\text{Trans} \begin{cases} K_1^a = 2.52 \times 10^{-4} \\ K_2^a = 5.60 \times 10^{-6} \\ K_1^a/K_2^a = 45 \end{cases}$$

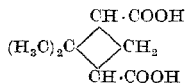
Cyclo-butane 1.3 dicarboxylic acid



$$\text{Cis} \begin{cases} K_1^a = 9.3 \times 10^{-5} \\ K_2^a = 4.9 \times 10^{-6} \\ K_1^a/K_2^a = 19 \end{cases}$$

$$\text{Trans} \begin{cases} K_1^a = 1.6 \times 10^{-4} \\ K_2^a = 5.3 \times 10^{-6} \\ K_1^a/K_2^a = 30 \end{cases}$$

Norpinic acid



$$\text{Cis} \begin{cases} K_1^a = 1.47 \times 10^{-4} \\ K_2^a = 2.84 \times 10^{-6} \\ K_1^a/K_2^a = 52 \end{cases}$$

$$\text{Trans} \begin{cases} K_1^a = 2.66 \times 10^{-4} \\ K_2^a = 5.73 \times 10^{-6} \\ K_1^a/K_2^a = 46 \end{cases}$$

It will be seen that the introduction of gemdimethyl group in *cis* caronic acid, tends to decrease the first dissociation constant and to increase the second, so that the ratio  $K_1^a/K_2^a$  for the isomer, becomes much smaller than the value of the unsubstituted acid. In other acids the gemdimethyl group affects the order of the dissociation constants in such a manner that the ratio  $K_1^a/K_2^a$  increases in all isomers. A similar increase in ratio has also been observed by Gane and Ingold (*Jour. Chem. Soc.*, 1928, 2267) in methyl substituted glutaric acids. It is surprising to see that the ratio  $K_1^a/K_2^a$  in the case of *cis* cyclo-butane acid obtained by Wasserman, is lower than the corresponding *trans* acid, which seems to be an error.

It is further evident that in *cis* acids, the ratio  $K_1^a/K_2^a$  is always higher than that for *trans* acids. The larger value of this ratio for *cis* acids is usually explained by the mutual influence of the adjacent carboxyl groups, so that when one of the group dissociates, the negative charge carried by the anion, exerts a force of repulsion on the negative charge carried by the other carboxyl group, and the second stage of ionisation is very much depressed. In *trans* acids, the two carboxyl groups, being wide apart, ionise practically independently of each other so that  $K_1^a$  and  $K_2^a$  are not very different.

Recently German, Jeffery and Vogel (*Jour. Chem. Soc.*, 1937, 1604) have also taken the ratio  $K_1^a/K_2^a$  as a criterion for differentiating between *cis* and *trans* acids.

Bjerrum (*Z. Physikal Chem.*, 1923, 106, 219) has suggested a semi-quantitative treatment of the relation of ratio  $K_1^a/K_2^a$  and the distance between the two carboxyl groups. In a symmetrical acid of the type H-A-A-H in which the two stages of ionisation proceed independently, the ratio  $K_1^a/K_2^a$  is 4 (Adams, *Jour. Amer. Chem. Soc.*, 1916, 38, 1503). In cases where there is a mutual influence between the two groups, the relation is given by the Bjerrum's formula,

$$K_1^a/K_2^a = 4 \log \frac{\epsilon}{DTkr}$$

where D is the dielectric constant of the medium, T the absolute temperature and  $r$  the distance between the two ionising groups,  $\epsilon$  is the electronic charge and  $k$ , the Boltzman's constant.

For aqueous solutions where  $D = 78.5$  the equation reduces to

$$n = (\log K_1 - \log K_2) - 0.6 = 3.1 \times 10^{-8}/r.$$

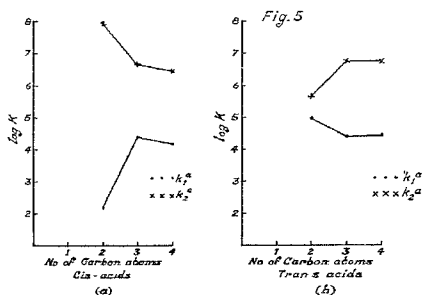
By applying the above equation, the values of  $r$  have been calculated for the acids under consideration and are given in the following table:—

Acid	$\log K_1^a$	$\log K_2^a$	$n$	$r \text{ \AA}$
<i>Cis</i> carbonic ..	$\bar{4}.384$	$\bar{6}.678$	1.106	2.80
<i>Trans</i> ..	$\bar{4}.401$	$\bar{6}.748$	1.053	2.94
<i>Cis</i> norpunic ..	$\bar{4}.167$	$\bar{6}.453$	1.114	2.78
<i>Trans</i> ..	$\bar{4}.425$	$\bar{6}.758$	1.067	2.91

The results show that the value of  $r$  for *trans* acids is greater than in the case of *cis* acids. Wasserman (*Helv. Chim. Acta.*,

1930, 13, 207, 223) has also obtained similar results in *cyclo*-propane, *cyclo*-butane and *cyclo*-pentane dicarboxylic acids. He has however taken the value of  $n$  as a measure of ring tension and has not discussed the values from the point of view of *cis-trans* configuration. According to him  $(\log K_1 - \log K_2) - 0.6 = n + x$ , where  $x$  depends on the atomic chain and the binding strength of the ring.

The values of  $\log K_1^c$  and  $\log K_2^c$  of these acids along with those of maleic and fumaric acids are plotted against the number of carbon atoms in the ring in Fig. 5 *a* and *b*. It is seen that for *cis* acids the



first dissociation constant decreases with an increase in carbon atoms from 2 to 3, and then remains almost constant and the second dissociation constants increases, with the number of carbon atoms. A reverse of this is observed in *trans* acids.

It should ordinarily be expected that the cyclic polymethylene dicarboxylic acid should have nearly the same dissociation constants as the corresponding straight chain polymethylene dicarboxylic acids. This, however, is not true because of the influence of strain in the ring in the former. If a comparison of the dissociation constants of these acids is made with those of glutaric acid, which are given by Gane and Ingold (*Jour. Chem. Soc.*, 1928, 1594), it is seen that the strain in the ring alters the order of the second dissociation constant only in the case of *cis* cyclo-propane dicarboxylic acid, where the strain is maximum and the two carboxyl groups are quite near. The strain in the ring, however, tends to increase the first stage of ionisation. Proceeding to higher homologous derivatives, the acids become more strainless, and in the *cyclo*-pentane acids, both the dissociation constants are of the same order as glutaric and adipic acids

(*cf.* Wasserman, *loc. cit.*; Ingold and Mohrhem, *Jour. Chem. Soc.*, 1935, 949).

Thanks of the authors are due to Dr. P. C. Guha for supplying the samples of acids used in this investigation.

### SUMMARY.

The primary and secondary dissociation constants of *cis* and *trans* caronic, *cis* and *trans* norpinic acids have been measured from the potentiometric titration data. The range over which the two acid groups titrate simultaneously is found to be 70% in the case of *cis* acids and 75% in *trans* acids.

The value of  $r$ , the distance between the two ionising groups, has been calculated by applying Bjerrum's formula and is found to be less in *cis* acids than in *trans* acids.

The importance of the ratio  $K_1^c/K_2^c$  as a criterion for distinguishing the *cis-trans* acids has been pointed out.

Department of General Chemistry,  
Indian Institute of Science,  
Bangalore (India).

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