The Dissociation Constants of Carboxytropone and Carboxytropolones

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Although tropolones possess the properties characteristic of enols and phenols, they may be regarded, in respect of acidity, as vinylogs of carboxylic acids. Their dissociation constants are closer to the latter than to those of phenols[1-4]. This is attributed to the resonance of the ions A and B. However, the acidity is not so enhanced as would be expected from the stabilization of the ion species A and B. This fact has been explained by considering the "aromatic" resonance of the species C and D, the former being less favored than the latter[2].

A B C D

In this study, the dissociation constants of 2-carboxytropone, 3-carboxytropolone and its derivatives have been determined by potentiometric titrations with a glass electrode. From the results obtained, the chelation between the substituted carboxyl group and the hydroxyl group of tropolones is discussed.

Experimental

Materials.—Eight compounds that were investigated in the present study were prepared in this laboratory and had the properties given in Table I. Ten milligrams of each compound was weighed accurately and dissolved in redistilled water ($\kappa<10^{-6}$mho/cm.) to prepare a solution of approximately 10^{-3} mole/l. in concentration (Table I). A 0.01 M carbonate-free sodium hydroxide solution was prepared by the usual method[16], and its concentration was standardized against recrystallized oxalic acid. The solution was kept in a bottle with a buret which had an arrangement for protection against carbon dioxide.

Three buffer solutions recommended by the National Bureau of Standards (U. S. A.)[17] were employed for the standard for the pH measurement. They are 0.05 M potassium hydrogen phthalate of pH 4.008 at 25°C, 0.025 M potassium

TABLE I

CARBOXYTROPONE AND CARBOXYTROPOLONES INVESTIGATED

No.	Compound	Molecular weight	M. p., °C	Conc. of soln., mM	Reference
1	2-Carboxytropone	150.13	148 (decomp.)	0.574	5
2	3-Carboxytropolone	166.13	218 (decomp.)	1.004	6, 7
3	4-Carboxytropolone	166.13	218	1.194	8, 9, 10
4	5-Carboxytropolone	166.13	290 (decomp.)	0.461	9, 11
5	3-Carboxy-4-methyltropolone	180.15	196 (decomp.)	1.001	12, 13
6	3-Carboxymethyltropolone	180.15	174 (decomp.)	1.001	14
7	Anhydride of 3,4-dicarboxytropolone[a]	192.12	254	0.825	12, 15
8	3-Carboxy-4-carboxymethyltropolone	244.16	183 (decomp.)	1.018	10, 12

a) This substance gives 3,4-dicarboxytropolone when dissolved in water.

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dihydrogen phosphate and 0.025 M disodium hydrogen phosphate of pH 6.857 at 25°C and 0.05 M borax of pH 9.180 at 25°C.

Apparatus and Procedure.—The cell

$$\text{Ag-AgCl}\left|\begin{matrix}0.1\,\text{M HCl}\\ (\text{inner})\end{matrix}\right|\begin{matrix}\text{glass}\\ \text{membrane}\end{matrix}\left|\begin{matrix}\text{sample solution}\\ +\text{NaOH}\\ (\text{outer})\end{matrix}\right|\begin{matrix}\text{saturated}\\ \text{KCl}\end{matrix}\left|\,\text{Hg}_2\text{Cl}_2\text{-Hg}\right.$$

was constructed for the pH measurement. The glass electrode which was designed by one of the authors (I. T. O.) had the shape of a small flask of approximately 30 ml. capacity. A standardized 0.1 M hydrochloric acid was placed inside. A titration cell used is shown in Fig. 1.

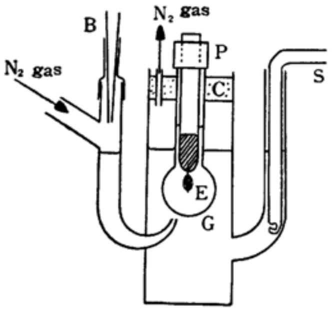

Fig. 1. Schematic diagram of the titration cell: G, glass membrane; E, silver-silver chloride electrode: P, polyethylene seal; C, cork; S, salt bridge; B, buret.

The pH of the solution was determined by the measurement of the electromotive force (e. m. f.) of the above cell. The measurement of e. m. f. was made by means of an instrument which consisted of a potentiometer and the combination of a UX-54 type vacuum tube (corresponding to the FP-54 type vacuum tube in the United States) and a galvanometer[18].

In order to remove the dissolved carbon dioxide and to stir the solution, purified nitrogen gas was passed through the solution before the titration and also after every addition of sodium hydroxide solution during the titration. The e. m. f. was measured with an accuracy of 0.0001 volt; therefore the pH was determined with an accuracy of 0.005 pH-unit. All measurements were carried out in a thermostat of 25.00±0.01°C.

Results

Titration Curves. — Typical titration curves obtained are reproduced in Fig. 2.

Calculation of Dissociation Constants.—(a) *Monobasic acid* (*HA*).—The dissociation constant of a monobasic acid, K_1, was calculated with the equation

$$K_1=\frac{a_{H^+}\times a_{A^-}}{a_{HA}}=\frac{a_{H^+}\left(b+\dfrac{a_{H^+}}{f_{H^+}}\right)f_{A^-}}{c-\left(b+\dfrac{a_{H^+}}{f_{H^+}}\right)}\qquad(1)$$

where c means the total concentration of an acid titrated, b the concentration of sodium hydroxide added, a_{H^+}, a_{HA} and a_{A^-} mean the activities of the hydrogen ion, the undissociated acid and the dissociated acid anion, respectively, and f_{H^+} and f_{A^-} the activity coefficients of the hydrogen ion and the dissociated acid anion, respectively. The activity coefficient of the undissociated acid HA was assumed to be unity, while those of the dissociated acid anion A^- and the hydrogen ion were calculated with the equation

$$\log f_i=-\frac{0.358Z_i^2\sqrt{\Gamma}}{1+0.2325a_i\times10^8\sqrt{\Gamma}}\qquad(2)$$

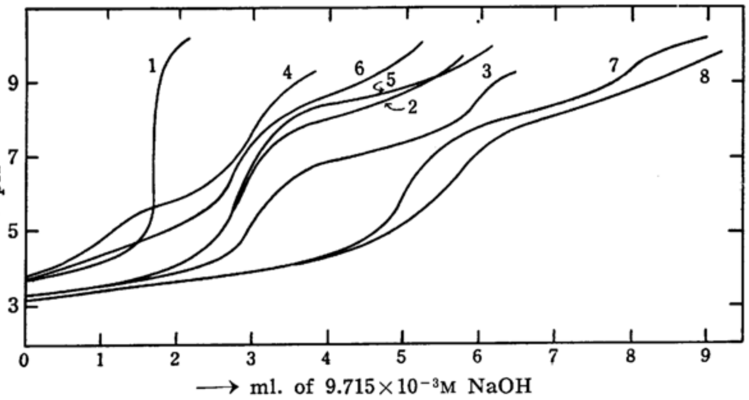

Fig. 2. Titration curves of carboxytropone and carboxytropolones. The curves are given the same number as in Table I.

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[18] N. Tanaka, I. T. Oiwa and M. Kodama, *Anal. Chem.*, **28**, 1555 (1956).

where Z_i represents the ionic charge, Γ the total ionic concentration, and a_i the ion-size parameter[19]. Because 2-carboxytropone was considered to have a molecular volume similar to that of benzoic acid, its ion-size parameter was assumed to be 6 Å according to Kielland's[19] tables.

(b) *Dibasic acids* (H_2A).—When $K_1/K_2 \geqq 10^3$, the first dissociation constant, K_1, was calculated with eq. 1 in which f_{A^-} was replaced by f_{HA^-}, the effect of the second dissociation being neglected. In this calculation, the part of the titration curve before the equivalence point for the first dissociation was used. The second dissociation constant, K_2, was calculated with the equation

$$K_2=\frac{a_{H^+}\times a_{A^{2-}}}{a_{HA^-}}=\frac{a_{H^+}\left(b+\dfrac{a_{H^+}}{f_{H^+}}-[\mathrm{OH}^-]\right)f_{A^{2-}}}{\left(2c+[\mathrm{OH}^-]-\dfrac{a_{H^+}}{f_{H^+}}-b\right)f_{HA^-}} \tag{3}$$

from the observed values which were obtained between the equivalence points for the first and the second dissociations on the titration curve.

(c) *Tribasic acids* (H_3A). — From the titration curves given in Fig. 2 it was seen that K_1/K_2 is not greater than 10^3, so that K_1 and K_2 were not able to be calculated by the procedure given in (b). In this case they were calculated with the equations

$$K_1K_2=\frac{a_{H^+}{}^2\times a_{HA^{2-}}}{a_{H_3A}}=a_{H^+}{}^2\left(\frac{b+\dfrac{a_{H^+}}{f_{H^+}}-[\mathrm{OH}^-]}{2c-b-\dfrac{a_{H^+}}{f_{H^+}}+[\mathrm{OH}^-]}\right)\times\left\{1+\frac{K_1f_{H^+}}{a_{H^+}}\left(\frac{b-c+\dfrac{a_{H^+}}{f_{H^+}}-[\mathrm{OH}^-]}{b+\dfrac{a_{H^+}}{f_{H^+}}-[\mathrm{OH}^-]}\right)\right\}f_{HA^{2-}} \tag{4}$$

$$K_1=a_{H^+}\left(\frac{b+\dfrac{a_{H^+}}{f_{H^+}}-[\mathrm{OH}^-]}{c-b-\dfrac{a_{H^+}}{f_{H^+}}-[\mathrm{OH}^-]}\right)\times\left\{1-K_1K_2\left(\frac{f_{H^+}}{a_{H^+}}\right)^2\left(\frac{2c-b-\dfrac{a_{H^+}}{f_{H^+}}+[\mathrm{OH}^-]}{b+\dfrac{a_{H^+}}{f_{H^+}}-[\mathrm{OH}^-]}\right)\right\}f_{H_2A^-} \tag{5}$$

from the values obtained before the equivalence point for the second dissociation on the titration curve.

The third dissociation constant, K_3, was calculated with the equation,

$$K_3=\frac{a_{H^+}\times a_{A^{3-}}}{a_{HA^{2-}}}=\frac{a_{H^+}\left(b+\dfrac{a_{H^+}}{f_{H^+}}-[\mathrm{OH}^-]\right)f_{A^{3-}}}{\left(3c-b-\dfrac{a_{H^+}}{f_{H^+}}+[\mathrm{OH}^-]\right)f_{HA^{2-}}} \tag{6}$$

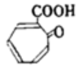
from the values obtained between the equivalence points for the second and third dissociations on the titration curve.

In Table II are given the typical examples of calculation for the mono- and di-basic acid, and in Table III, the dissociation constants obtained for the compounds investigated. For comparison, the dissociation constants of several substances which have structures similar to the compounds investigated in this study are also given in Table III.

Discussion

2-Carboxytropone (E_1). — This acid is stronger than benzoic acid. This is attributed to the fact that the inductive (electron withdrawal) effect of a tropone ring is stronger than that of a benzene ring.

3-Carboxytropolone (E_2) and 3-carboxy-4-methyltropolone (E_5). — The values of pK_1 are smaller than those of benzoic acid and 2-carboxytropone. This shows the stronger inductive effect of the tropolone ring as well as the existence of chelation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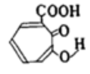
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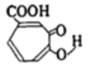
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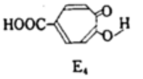
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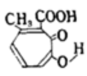
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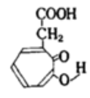
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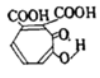
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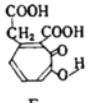
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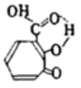
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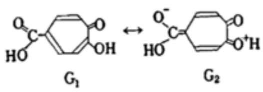
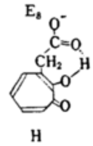

G_1 G_2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[19] J. Kielland, *J. Am. Chem. Soc.*, **59**, 1675 (1937).

TABLE II

RESULTS OF TITRATION

2-Carboxytropone with 9.715×10^{-3}M NaOH

NaOH, ml.	pH	$a_{H^+}\times10^4$	f_{H^+}	$b\times10^4$	$[A^-]\times10^4$	f_{A^-}	$K_1\times10^4$
0.14	3.66	2.18_3	0.982	0.448	2.592	0.982	1.88
0.31	3.73	1.86_2	.981	0.993	2.890	.981	1.89
0.57	3.85	1.39_0	.980	1.811	3.229	.980	1.82
0.75	3.95	1.12_2	.979	2.369	3.515	.979	1.85
0.91	4.04	0.91_2	.978	2.860	3.791	.978	1.89
1.10	4.18	0.65_4	.977	3.436	4.105	.977	1.82
						mean	1.86
							$pK_1=3.73\pm0.01$

3-Carboxytropolone with 9.715×10^{-3}M NaOH

NaOH, ml.	pH	$a_{H^+}\times10^4$	f_{H^+}	$b\times10^4$	$[HA^-]\times10^4$	f_{HA^-}	$K_1\times10^4$
0.15	3.30	5.01_2	0.973	0.483	5.623	0.973	6.28
0.42	3.35	4.41_6	.973	1.341	5.877	.973	6.26
0.61	3.39	3.99_9	.973	1.951	6.060	.973	6.22
0.88	3.46	3.46_8	.973	2.768	6.326	.973	6.23
1.12	3.52	3.02_0	.972	3.496	6.601	.972	6.28
						mean	6.25
							$pK_1=3.20\pm0.01$

NaOH, ml.	pH	$a_{H^+}\times10^9$	f_{H^+}	$b\times10^4$	$[HA^-]\times10^4$	f_{HA^-}	$[A^{2-}]\times10^4$	$f_{A^{2-}}$	$[OH^-]\times10^6$	$K_2\times10^8$
4.46	8.29	5.12	0.944	12.57	4.939	0.941	12.55	0.787	1.79_7	1.08
4.64	8.38	4.16	.943	13.01	4.417	.941	12.98	.785	2.66_7	1.02
4.93	8.65	2.23	.942	13.71	3.591	.940	13.66	.782	4.22_1	1.02
									mean	1.04
										$pK_2=7.98\pm0.01$

TABLE III

DISSOCIATION CONSTANTS OF CARBOXYTROPONE, CARBOXYTROPOLONES AND THE RELATED COMPOUNDS

Compound	pK_1	pK_2	pK_3
2-Carboxytropone	3.73 ± 0.01		
3-Carboxytropolone	3.20 ± 0.01	7.98 ± 0.01	
4-Carboxytropolone	3.42 ± 0.005	7.03 ± 0.01	
5-Carboxytropolone	4.05 ± 0.01	6.41 ± 0.02	
3-Carboxy-4-methyltropolone	3.15 ± 0.01	8.29 ± 0.01	
3-Carboxymethyltropolone	4.52 ± 0.02	8.77 ± 0.05	
3, 4-Dicarboxytropolone	3.24 ± 0.03	6.26 ± 0.03	8.57 ± 0.01
3-Carboxy-4-carboxymethyltropolone	3.75 ± 0.03	5.90 ± 0.05	8.08 ± 0.02
Acetic acid	4.756 20)		
Benzoic acid	4.201 20)		
Tropolone	6.92 3)		
4-Methyltropolone	7.26 3)		

such as given in structure F. The larger values of pK_2 also show the existence of stable chelation.

4-Carboxytropolone (E_3) and 5-carboxytropolone (E_4). — In these substances the carboxyl group will not be able to form the chelation of type F, which 3-carboxytropolone forms. The magnitudes of pK_1 of these acids, therefore, are expected to be larger than those of 3-carboxytropolone and 3-carboxy-4-methyltropolone, and the magnitudes of pK_2 of the former, smaller than those of the latter. The experimental results agree with this expectation; The pK_1 of 5-carboxytropolone is much greater than that of 4-carboxytropolone, this may be attributed to the contribution of structure G_2. It is also interesting to notice that the difference between pK_1

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20) R. A. Robinson and R. H. Stokes, "Electrolytic Solutions," Butterworths Scientific Publications, London, p. 436 (1955).

and pK_2 of 5-carboxytropolone is much smaller than the differences of other monocarboxytropolones (See Table III).

3-Carboxymethyltropolone (E_6). — The methylene group shields the inductive effect of a tropolone ring upon the carboxyl group, and, consequently, the pK_1 value is close to that of acetic acid. The large pK_2 value indicates the existence of the stable chelation (structure H).

3, 4-Dicarboxytropolone (E_7) **and 3-carboxy-4-carboxymethyltropolone** (E_8).— 3, 4-Dicarboxytropolone gives a pK_1 value which is nealy equal to that of 3-carboxytropolone (E_2), while 3-carboxy-4-carboxymethyltropolone gives a somewhat larger pK_1. This seems to be due to the greater steric interference of a carboxymethyl group in the 4-position.

Summary

The thermodynamic dissociation constants of 2-carboxytropone, 3-carboxytropolone, 4-carboxytropolone, 5-carboxytropolone, 3-carboxy-4-methyltropolone, 3-carboxymethyltropolone, 3, 4-dicarboxytropolone and 3-carboxy-4-carboxymethyltropolone have been determined by means of the pH titration with a glass electrode.

The relationships between the magnitudes of the dissociation constants and the structures of these compounds have been discussed.

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