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The Stability Constants of Squaric Acid and Rhodizonic Acid

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Emf methods have been used to determine the stability constants of squaric acid (3,4-dihydroxy-3-cyclobutene-1,2-dione) in an ionic medium of 3 M $NaClO_4$ at 25°C. To determine the stability constants of rhodizonic acid, emf and spectrophotometric methods have been used, all measurements having been performed in the same ionic medium. Preliminary constants were obtained graphically by curve fitting methods and were then refined by the generalized least squares program LETAGROP. The experimental data could best be explained in terms of the following equilibria and corresponding stability constants:

	Emf	Spectr.
$H^+ + C_4O_4^{2-} \rightleftharpoons HC_4O_4^-$	$\log \beta_1 = 3.19 \pm 0.01$	–
$2H^+ + C_4O_4^{2-} \rightleftharpoons H_2C_4O_4$	$\log \beta_2 = 4.15 \pm 0.02$	–
$H^+ + C_6O_6^{2-} \rightleftharpoons HC_6O_6^-$	$\log \beta_1 = 3.58 \pm 0.05$	3.1 ± 0.5
$2H^+ + C_6O_6^{2-} \rightleftharpoons H_2C_6O_6$	$\log \beta_2 = 7.03 \pm 0.06$	7.0 ± 0.3

The errors given correspond to an error of 3σ in β, where σ is the standard deviation in β.

The anions, $C_nO_n^{2-}$, of squaric acid (3,4-dihydroxy-3-cyclobutene-1,2-dione, $H_2C_4O_4$), croconic acid (4,5-dihydroxy-4-cyclopentene-1,2,3-trione, $H_2C_5O_5$), and rhodizonic acid (5,6-dihydroxy-5-cyclohexene-1,2,3,4-tetrone, $H_2C_6O_6$), have been investigated by West and Powell [1] and shown to be aromatic (*cf.* Fig. 1).

Methods for the synthesis of rhodizonates [2] and croconates [3] have been known for a long time, but it was not possible to prepare squarates until squaric acid was synthetized in 1959 by Cohan *et al.*[4] Whereas aqueous solutions of squaric acid and its salts are comparatively stable, those of rhodizonic acid and rhodizonates are unstable. Rhodizonates can therefore seldom be obtained in a pure form, since recrystallization cannot be used for purification.[2]

In 1938, Carpéni [5] determined the acidity constants of rhodizonic acid and croconic acid. Although his values for croconic acid ($pK_{a1} = 2.17$ and

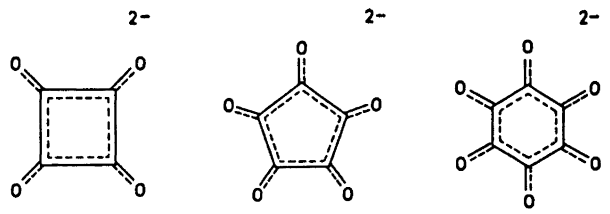

Fig. 1. The bonding systems in the A^{2-} anions of squaric acid, croconic acid, and rhodizonic acid.

$pK_{a2} = 4.0$) differ considerably from those reported by Carlqvist and Dyrssen [6] ($pK_{a1} = 0.32$ and $pK_{a2} = 1.51$), those for rhodizonic acid ($pK_{a1} = 3.15$ and $pK_{a2} = 4.9$) were later confirmed by Schwarzenbach and Suter [7] ($pK_{a1} = 3.15$ and $pK_{a2} = 4.9$). The values reported by Preisler *et al.*[8] for rhodizonic acid ($pK_{a1} = 4.1$ and $pK_{a2} = 4.5$) diverge, however, from these values as do the values ($pK_{a1} = 4.20$ and $pK_{a2} = 4.65$) reported by Takahashi *et al.*[9] Banerje *et al.*[10] have, on the other hand, reported a higher value ($pK_{a2} = 5.06$) for the second acidity constant.

The acidity constants of squaric acid have been determined in solutions with low varying ionic strengths by Ireland and Walton [11] ($pK_{a1} = 1.7$ and $pK_{a2} = 3.21$), by Tedesco and Walton [12] ($pK_{a1} = 0.4$ and $pK_{a2} = 2.89$), by MacDonald [13] ($pK_{a1} = 1.2$ and $pK_{a2} = 3.48$) and by Park *et al.*[14] ($pK_{a2} = 3$).

It is well known that the anions of the acids $H_2C_nO_n$ form strong metal complexes. Carlqvist and Dyrssen [15] have determined the stability constants for the formation of CaC_5O_5, SrC_5O_5, and BaC_5O_5, and Al-Mahdi and Schönfeld [16] have used rhodizonic acid solutions to eluate yttrium from anion exchange columns. The latter authors showed that anionic yttrium rhodizonate complexes, *e.g.* $[Y(C_6O_6)_3]^{3-}$ were formed. Tedesco and Walton [12] have determined formation constants for squarate complexes of iron(III), uranium(VI), aluminium(III), copper(II), manganese(II), cobalt(II), and nickel(II).

In order to be able to determine the stability constants of metal complexes of these acids, their acidity constants must be accurately known. An ionic medium of high ionic strength must be used to keep the activity coefficients constant during the experiments. In this work 3 M $NaClO_4$ was chosen since many recent investigations of stability constants have been carried out in this medium. As no acidity constants for squaric acid and rhodizonic acid have been determined in 3 M $NaClO_4$, it was necessary to commence the investigation with their determination.

EXPERIMENTAL

Chemicals. Perchloric acid (Merck, *p.a.*) was standardized against thallium carbonate (BDH).

Sodium perchlorate was prepared from sodium carbonate (Merck, *p.a.*) and perchloric acid as described by Biederman.[17]

Sodium rhodizonate solutions were freshly made for each experiment by dissolving a calculated quantity of $Na_2C_6O_6$ (Merck, *p.a.*) in doubly distilled water, saturated with gaseous nitrogen. During the dissolution a stream of nitrogen was passed through the

solution, since rhodizonate solutions decompose in contact with air. The commercial product was analysed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark. (Found: C 31.3; H 0.37; Na 22.0 Calc. for $Na_2C_6O_6$: C 33.7; H 0.0; Na 21.5.) Recrystallization could not be carried out owing to the instability of the aqueous solutions.[3] The salt was examined by NMR methods but no acetate, ethanol, or other substance containing C–H bonds, soluble in D_2O, could be detected.

Squaric acid was kindly prepared by Dr. Kåre Olsson from 1,2-dichloro-3,3,4,4-tetrafluorocyclobutene (K & K) according to the method described by West *et al.*[18]

Sodium squarate was also prepared by Olsson by dissolving squaric acid in a hot solution of sodium hydroxide (Bohus EKA, *p. a.*) and precipitating the salt by cooling. Sodium squarate was recrystallized from water. (Found: C 22.9; H 2.82. Calc. for $Na_2C_4O_4 \cdot 3H_2O$: C 22.7; H 2.85.)

Apparatus. A cell of the following type was used for the emf measurements:

–glass electrode	equilibrium solutions, S	3000 mM $NaClO_4$	10 mM $AgClO_4$ 2990 mM $NaClO_4$	AgCl(s)	Ag(s)+

The vessels used for the salt bridge and the reference electrode were of the Wilhelm type.[19] The glass electrodes were Beckman 40495, calibrated according to the method described by Olin.[20] The silver/silver chloride electrodes were prepared by Brown's method.[21] The cell was immersed in a paraffin oil thermostat at 25.0 ± 0.1°C in a room thermostated to 25°C. The emf of the cell was measured with a Radiometer PHM 4 (accuracy ± 0.2 mV) and in some titrations with a Radiometer PHM 52 (accuracy ± 0.1 mV). A stream of nitrogen gas, taken from cylinders and purified by passing first through a column containing activated copper and then through four bottles containing 10 % H_2SO_4, 10 % NaOH, 3 M $NaClO_4$, and 3 M $NaClO_4$, respectively, was used to stir the solution S.

The *light absorption measurements* at constant wavelength were performed on a Beckman spectrophotometer, Model DU-2, after the spectra had been recorded with a Beckman recording spectrophotometer, Model DB. Fused quartz cells with the path lengths 0.1, 0.2, 0.5, 1.0 cm were employed and these were calibrated before use. During the measurements the sample compartment was thermostated to 25.0 ± 0.1°C. The solutions used in the spectrophotometric measurements were prepared by mixing solutions of sodium rhodizonate with perchloric acid, the ionic strength being held at 3 M by the addition of sodium perchlorate. The free hydrogen ion concentration in each solution was measured according to the emf method described below.

EMF MEASUREMENTS

The experiments were carried out as a series of emf titrations at a constant total concentration, B, of the acid, the total hydrogen ion concentration, H, varying in each titration. The equilibrium solutions S thus had the composition B mM Na_2A, H mM $HClO_4$, $(3000 - 2B - H)$ mM $NaClO_4$, where A^{2-} represents the divalent anion of the acid. Since the solubilities of the sodium salts of these acids are slight, the values of B were limited to the range 2 mM $< B <$ 7 mM for squarates and to 0.5 mM $< B <$ 2 mM for rhodizonates.

As usual, the free hydrogen ion concentration, h, was calculated from the measured emf, by means of the equation

$$E = E_0 - \frac{RT \ln 10}{F} \log h + E_j$$

where E_0 is a constant for the electrodes used and E_j is the liquid junction potential. According to Biederman and Sillén,[22] E_j can be expressed as a function of h, *i.e.* $E_j = jh$, where j is a constant.

E_0 and j were determined, in accordance with Ref. 22, by means of independent H^+ titrations in 3 M $NaClO_4$ with $B=0$ immediately before and after each main titration, in which $B\neq 0$.

TREATMENT OF EMF DATA AND RESULTS

During the titrations the A^{2-} anions take part in the following reactions

$$H^+ + A^{2-} \rightleftharpoons HA^- \quad (1)$$

$$2H^+ + A^{2-} \rightleftharpoons H_2A \quad (2)$$

The equilibrium constants for these reactions are denoted by β_1 and β_2, respectively. The average number, $\bar{n}$, of hydrogen ions bound to each A^{2-} added is then given by the following equation:

$$\bar{n} = \frac{2[H_2A] + [HA^-]}{B} = \frac{2\beta_2 h^2 + \beta_1 h}{1 + \beta_1 h + \beta_2 h^2} \quad (3)$$

where $[H_2A] = \beta_2 h^2 [A^{2-}]$ and $[HA^-] = \beta_1 h [A^{2-}]$ have been introduced according to (1) and (2). From the stoichiometric relation

$$2[H_2A] + [HA^-] = H - h \quad (4)$$

$\bar{n}$ can be obtained as

$$\bar{n} = \frac{H - h}{B} \quad (5)$$

and can thus be calculated from the experimental data as a function of log h (*cf.* Tables 1 and 2). This function is shown in Fig. 2 (for squaric acid) and in Fig. 3 (for rhodizonic acid). As is seen in Fig. 3, $\bar{n}$ decreases in some of the rhodizonic acid titrations when pH < 2.7. This is probably due to the decomposition of rhodizonic acid whereas its anions seem to be fairly stable under the experimental conditions used.

The squaric acid titrations were terminated at pH≈1.4 (*cf.* Fig. 2) since the experimental accuracy decreased very rapidly at pH values less than 1.5.

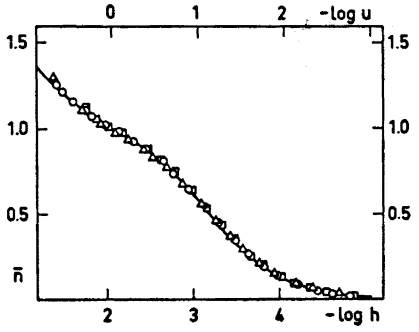

Fig. 2. $\bar{n}$ data as a function of $-\log h$ for squaric acid. The values for B are □ 6.054 mM, ○ 5.501 mM, and △ 4.395 mM. The curve drawn is the normalized curve $\bar{n} = f(\log u)_R$ with $R = 12$.

Table 1. Emf data for squaric acid. The four columns give the values for E, $H \times 10^3$, $\log h$, and $\bar{n}$, respectively. The potentials are expressed in mV and the concentrations in M. In the calculation of E_j, $j = 16.5$ mV M^{-1} was used.

B = 0.004188

E_0 = 35.68

-347.50	0.03	-6.478	0.007
-263.00	0.10	-5.049	0.022
-243.80	0.17	-4.725	0.036
-233.00	0.24	-4.542	0.051
-219.00	0.38	-4.305	0.080
-209.60	0.52	-4.146	0.108
-199.10	0.73	-3.969	0.149
-188.80	1.00	-3.795	0.201
-179.30	1.36	-3.634	0.270
-168.70	1.86	-3.455	0.361
-157.90	2.45	-3.272	0.457
-148.10	3.15	-3.107	0.565
-136.50	4.05	-2.910	0.673
-125.10	5.16	-2.717	0.775
-114.70	6.44	-2.541	0.851
-104.70	8.10	-2.372	0.919
-94.90	10.20	-2.206	0.948
-85.60	13.23	-2.048	1.020
-75.90	17.51	-1.883	1.053
-69.60	21.38	-1.775	1.096
-64.40	25.40	-1.686	1.147

B = 0.005501

E_0 = 35.86

-358.80	-0.03	-6.672	-0.006
-255.00	0.07	-4.917	0.011
-237.30	0.20	-4.618	0.033
-226.70	0.32	-4.439	0.051
-212.50	0.55	-4.198	0.089
-199.10	0.87	-3.972	0.139
-189.60	1.20	-3.811	0.190
-179.70	1.67	-3.644	0.262
-170.00	2.21	-3.480	0.341
-159.20	2.91	-3.297	0.438
-147.40	3.83	-3.098	0.551
-138.40	4.66	-2.946	0.641
-128.40	5.70	-2.776	0.732
-119.10	6.87	-2.619	0.811
-108.80	8.42	-2.444	0.878
-100.30	10.11	-2.300	0.927
-90.20	12.83	-2.129	0.982
-82.30	15.73	-1.995	1.019
-72.30	20.87	-1.824	1.070
-66.20	25.32	-1.720	1.139

B = 0.004188

E_0 = 35.41

-364.90	0.03	-6.767	0.007
-245.70	0.17	-4.752	0.037
-227.30	0.32	-4.441	0.068
-206.80	0.61	-4.094	0.126
-194.70	0.89	-3.890	0.182
-185.50	1.18	-3.734	0.237
-174.90	1.61	-3.555	0.318
-163.90	2.17	-3.369	0.416
-154.60	2.72	-3.212	0.504
-143.10	3.55	-3.017	0.618
-132.10	4.47	-2.831	0.716
-121.90	5.56	-2.659	0.802
-112.90	6.74	-2.506	0.866
-103.90	8.24	-2.354	0.911
-96.40	9.94	-2.227	0.956
-89.90	11.80	-2.116	0.991
-83.70	14.00	-2.011	1.015
-76.90	17.14	-1.895	1.052
-68.30	22.47	-1.748	1.103
-58.60	31.15	-1.582	1.185

B = 0.006054

E_0 = 35.92

-352.40	0.03	-6.564	0.005
-251.40	0.16	-4.857	0.024
-233.10	0.28	-4.548	0.042
-222.10	0.46	-4.362	0.068
-210.80	0.66	-4.171	0.097
-202.80	0.85	-4.035	0.126
-189.10	1.39	-3.804	0.203
-180.20	1.79	-3.653	0.260
-170.20	2.42	-3.484	0.346
-160.80	3.08	-3.325	0.431
-150.70	3.92	-3.155	0.532
-139.90	4.91	-2.972	0.636
-129.60	6.05	-2.798	0.736
-119.90	7.24	-2.633	0.811
-110.20	8.72	-2.469	0.879
-99.00	12.51	-2.178	0.968
-83.40	15.78	-2.014	1.009
-75.50	19.55	-1.880	1.051
-68.70	24.01	-1.764	1.120

B = 0.004395

E_0 = 41.73

-369.00	0.03	-6.943	0.007
-237.40	0.18	-4.719	0.037
-218.00	0.33	-4.391	0.066
-206.90	0.48	-4.203	0.095
-192.10	0.78	-3.953	0.152
-181.90	1.07	-3.780	0.207
-170.40	1.52	-3.586	0.286
-161.40	1.99	-3.434	0.368
-151.30	2.57	-3.263	0.460
-141.10	3.25	-3.090	0.556
-128.90	4.27	-2.884	0.675
-117.80	5.38	-2.696	0.767
-108.80	6.47	-2.544	0.822
-101.90	7.59	-2.427	0.877
-91.60	9.67	-2.252	0.928
-81.80	12.46	-2.086	0.967
-73.00	16.06	-1.936	1.020
-59.90	24.24	-1.713	1.105
-37.10	53.63	-1.319	1.293

B = 0.005860

E_0 = 42.15

-372.20	0.03	-7.004	0.005
-264.00	0.09	-5.175	0.015
-245.10	0.16	-4.856	0.024
-234.10	0.22	-4.670	0.034
-226.30	0.28	-4.538	0.043
-215.20	0.41	-4.350	0.062
-207.20	0.53	-4.215	0.080
-198.00	0.78	-4.060	0.118
-190.90	1.00	-3.940	0.151
-183.50	1.27	-3.815	0.190
-174.30	1.70	-3.659	0.253
-160.70	2.52	-3.429	0.366
-151.80	3.20	-3.279	0.455
-142.20	3.96	-3.116	0.546
-131.90	4.96	-2.942	0.651
-120.90	6.15	-2.756	0.749
-112.20	7.26	-2.609	0.818
-104.30	8.44	-2.475	0.868
-97.60	9.74	-2.361	0.919
-90.70	11.32	-2.244	0.959
-84.10	13.19	-2.132	0.992
-78.60	15.14	-2.039	1.023
-71.90	18.04	-1.925	1.049

B = 0.005501

E_0 = 35.98

-327.80	-0.03	-6.150	-0.006
-252.20	0.09	-4.872	0.014
-234.50	0.24	-4.572	0.039
-224.00	0.33	-4.395	0.053
-216.80	0.47	-4.273	0.075
-205.60	0.67	-4.084	0.106
-194.40	1.00	-3.894	0.158
-184.00	1.43	-3.719	0.225
-175.70	1.86	-3.578	0.290
-166.50	2.38	-3.423	0.364
-155.30	3.20	-3.233	0.476
-144.60	4.09	-3.052	0.582
-134.20	5.05	-2.876	0.677
-124.30	6.19	-2.709	0.769
-115.10	7.37	-2.553	0.831
-106.70	8.78	-2.411	0.889
-104.00	9.28	-2.365	0.903

B = 0.004687

E_0 = 35.56

-356.20	-0.03	-6.628	-0.008
-237.20	0.16	-4.611	0.030
-226.30	0.29	-4.427	0.053
-210.80	0.48	-4.165	0.089
-201.60	0.70	-4.009	0.129
-190.80	1.02	-3.827	0.185
-179.80	1.42	-3.641	0.254
-169.50	1.96	-3.466	0.345
-150.10	3.24	-3.138	0.535
-139.60	4.11	-2.961	0.644
-130.00	4.97	-2.798	0.720
-120.20	6.10	-2.632	0.805
-109.70	7.62	-2.455	0.876
-100.60	9.37	-2.300	0.931
-93.30	11.15	-2.176	0.958
-81.20	15.48	-1.971	1.021
-71.80	20.59	-1.811	1.092
-66.90	24.03	-1.727	1.125

B = 0.003142

E_0 = 44.53

-205.40	0.33	-4.225	0.087
-191.70	0.53	-3.993	0.136
-178.30	0.82	-3.767	0.206
-160.50	1.44	-3.466	0.349
-141.30	2.38	-3.141	0.528
-125.30	3.49	-2.871	0.680
-109.10	5.05	-2.596	0.800
-96.50	6.97	-2.383	0.901
-86.10	9.16	-2.207	0.937

Table 2. Emf data for rhodizonic acid. The four columns give the values for E, $H \times 10^3$, $\log h$, and $\bar{n}$, respectively. The potentials are expressed in mV and the concentrations in M. E_j has been neglected because of the low hydrogen ion concentrations.

B = 0.001097
E_0 = 37.1

-268.00	0.04	-5.158	0.030
-240.70	0.14	-4.696	0.112
-219.70	0.29	-4.341	0.224
-204.10	0.48	-4.077	0.358
-194.30	0.65	-3.912	0.484
-186.00	0.87	-3.771	0.640
-176.10	1.20	-3.604	0.868
-162.20	1.84	-3.369	1.284
-149.90	2.31	-3.161	1.478
-140.10	2.78	-2.996	1.614
-131.90	3.27	-2.857	1.712
-122.90	3.94	-2.705	1.789
-117.90	4.43	-2.620	1.856
-112.80	4.96	-2.534	1.859

B = 0.001092
E_0 = 37.6

-264.60	0.02	-5.109	0.016
-251.20	0.08	-4.882	0.064
-228.60	0.19	-4.500	0.148
-216.20	0.30	-4.290	0.225
-203.90	0.45	-4.082	0.334
-196.30	0.60	-3.954	0.451
-186.50	0.82	-3.788	0.601
-174.40	1.20	-3.584	0.860
-161.40	1.81	-3.364	1.262
-149.40	2.34	-3.161	1.512
-138.00	2.88	-2.968	1.653
-132.00	3.28	-2.867	1.762
-123.30	3.89	-2.720	1.817
-116.70	4.39	-2.608	1.762

B = 0.000896
E_0 = 38.4

-304.70	0.02	-5.800	0.021
-262.50	0.06	-5.087	0.058
-242.50	0.10	-4.749	0.092
-228.50	0.16	-4.512	0.144
-215.40	0.24	-4.290	0.206
-205.80	0.33	-4.128	0.284
-197.00	0.45	-3.979	0.387
-189.70	0.59	-3.856	0.507
-183.30	0.75	-3.748	0.639
-176.70	0.95	-3.636	0.797
-170.30	1.16	-3.528	0.962
-165.30	1.35	-3.443	1.104
-160.30	1.55	-3.359	1.239
-154.10	1.80	-3.254	1.386
-147.70	2.07	-3.146	1.513
-142.60	2.29	-3.060	1.589
-138.00	2.52	-2.982	1.644
-132.50	2.81	-2.889	1.695
-127.30	3.17	-2.801	1.773

B = 0.000504
E_0 = 39.4

-264.50	-0.01	5.137	-0.036
-253.70	0.01	-4.955	0.003
-235.70	0.06	-4.650	0.084
-221.30	0.12	-4.407	0.159
-212.70	0.18	-4.262	0.238
-201.00	0.26	-4.064	0.353
-189.50	0.41	-3.869	0.538
-178.00	0.60	-3.675	0.762
-165.20	0.90	-3.459	1.087
-154.10	1.22	-3.271	1.353
-143.80	1.58	-3.097	1.547
-137.00	1.87	-2.982	1.642
-131.40	2.15	-2.887	1.692

B = 0.001685
E_0 = 34.4

-318.90	0.00	-5.972	0.000
-273.30	0.06	-5.202	0.032
-259.80	0.11	-4.973	0.060
-247.60	0.16	-4.767	0.086
-234.70	0.23	-4.549	0.119
-225.00	0.34	-4.385	0.180
-213.90	0.49	-4.197	0.253
-203.00	0.73	-4.013	0.375
-193.00	1.02	-3.844	0.523
-184.10	1.38	-3.694	0.696
-173.00	1.96	-3.506	0.979
-163.30	2.55	-3.342	1.245
-152.60	3.18	-3.161	1.476
-140.80	3.88	-2.962	1.657
-131.10	4.54	-2.798	1.749
-128.20	4.85	-2.749	1.819

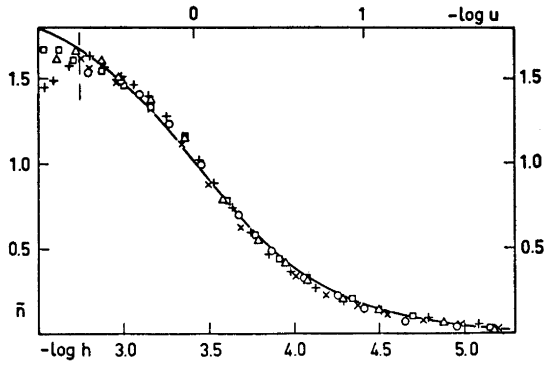

Fig. 3. $\bar{n}$ data as a function of $-\log h$ for rhodizonic acid. The values for B are × 1.895 mM, □ 1.219 mM, △ 1.199 mM, + 0.972 mM, and ○ 0.555 mM. The curve drawn is the normalized curve $\bar{n} = f(\log u)_R$ with $R = 1.7$.

In order to determine values of β_1 and β_2, the experimental curves in Figs. 2 and 3 were fitted to the following normalized curves:

$$n = \frac{Ru + 2u^2}{1 + Ru + u^2}$$

where $u = \beta_2^{\frac{1}{2}} h$ and $R = \beta_1 \beta_2^{-\frac{1}{2}}$ (Sillén's curve fitting method [23]). Functions $\bar{n} = \mathrm{f}(\log u)_R$ were drawn for different constant R values and compared with the experimental ones. The best fit was obtained when

$\log u = \log h + 2.06$, $R = 12$ (for squaric acid)

$\log u = \log h + 3.41$, $R = 1.7$ (for rhodizonic acid)

The following values were thus obtained for the stability constants:

$\log \beta_1 = 3.14$, $\log \beta_2 = 4.12$ (for squaric acid)

$\log \beta_1 = 3.64$, $\log \beta_2 = 6.82$ (for rhodizonic acid)

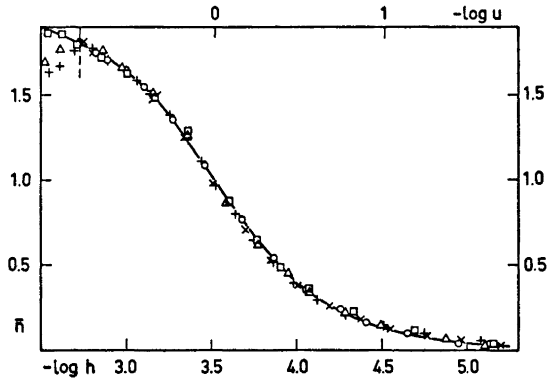

Fig. 4. $\bar{n}$ data as a function of $-\log h$ for rhodizonic acid. The $\bar{n}$ and $\log h$ values have been calculated from the same emf data as in Fig. 3 but with the corrected B values obtained from the LETAGROP calculations: × 1.685 mM, □ 1.097 mM, △ 1.092 mM, + 0.896 mM, and ○ 0.504 mM. The curve drawn is the normalized curve $\bar{n} = f(\log u)_R$ with $R = 1.2$.

In order to obtain more accurate results, the data were processed with the generalized least squares program LETAGROP.[24] Because of the discrepancies in the analysis of $Na_2C_6O_6$(s) and the instability of the solutions of rhodizonic acid and rhodizonates, it is possible that the total concentration, B, in each titration was not quite accurate. An allowance for an experimental error in B was therefore made in the LETAGROP calculations, the best fit being obtained, when B was multiplied by a factor which varied in the different titrations between 0.89 and 0.92. Attempts to adjust the B values in the squaric acid titrations did not, however, result in any improvement. During the calculations, the E_0 values were adjusted slightly but the H values were kept constant. The refinement of the constants gave the following "best values":

$$\begin{aligned} &\log(\beta_1 \pm 3\sigma) = 3.19 \pm 0.01 \\ &\log(\beta_2 \pm 3\sigma) = 4.15 \pm 0.02 \end{aligned} \quad \text{(for squaric acid)}$$

$$\begin{aligned} &\log(\beta_1 \pm 3\sigma) = 3.58 \pm 0.05 \\ &\log(\beta_2 \pm 3\sigma) = 7.03 \pm 0.06 \end{aligned} \quad \text{(for rhodizonic acid)}$$

where σ is the standard deviation in β. The error squares sums, defined as

$$U = \sum(H_{\text{calc}} - H)^2$$

were 0.312×10^{-6} for 173 titration points (squaric acid) and 0.077×10^{-6} for 76 titration points (rhodizonic acid). The stability constants are related as follows to the acidity constants:

$$\begin{aligned} &pK_{a1} = \log \beta_2 - \log \beta_1 = 0.96 \pm 0.03 \\ &pK_{a2} = \log \beta_1 = 3.19 \pm 0.01 \end{aligned} \quad \text{(for squaric acid)}$$

$$\begin{aligned} &pK_{a1} = \log \beta_2 - \log \beta_1 = 3.45 \pm 0.11 \\ &pK_{a2} = \log \beta_1 = 3.58 \pm 0.05 \end{aligned} \quad \text{(for rhodizonic acid)}$$

SPECTROPHOTOMETRIC MEASUREMENTS

Like most aromatic molecules, the squarate and rhodizonate ions absorb radiation in the ultraviolet or visible ranges. The absorbance can be used to determine the ion concentration and thus provides a useful method of determining the stability constants.

In order to find suitable wavelengths for the measurements, spectra were recorded for sodium rhodizonate solutions with constant B and varying h (*cf.* Fig. 5). The wavelengths 220 nm and 320 nm were then chosen for the accurate measurements. Although the absorbance is very strong at 470 nm, the wavelength used by Schwarzenbach and Suter,[7] it decreases rapidly. At 220 and 320 nm, however, the absorbance does not change appreciably during the time of measurement, although it slowly decreases after some hours. Thus the accuracy of the measurements is probably better at 220 and 320 nm than at 470 nm.

Absorbance measurements were made within 10 min of removal of the sample from the nitrogen atmosphere of the titration vessel. The absorbance was measured at a fixed wavelength using 3 M $NaClO_4$ as a blank.

TREATMENT OF THE SPECTROPHOTOMETRIC DATA AND RESULTS

The absorbance, A, of a solution is the product of the apparent molar absorptivity, ε, the optical pathlength, l, and the total concentration of the absorbing substance, B,

$$A = lB\varepsilon = l\,(\varepsilon_0[A^{2-}] + \varepsilon_1[HA^-] + \varepsilon_2[H_2A]) \tag{6}$$

where ε_0, ε_1, and ε_2 are the molar absorptivities for A^{2-}, HA^-, and H_2A, respectively. Inserting the formulae for $[HA^-]$, $[H_2A]$, and B into eqn. (6) gives

$$\varepsilon = \frac{\varepsilon_0 + \varepsilon_1 \beta_1 h + \varepsilon_2 \beta_2 h^2}{1 + \beta_1 h + \beta_2 h^2} \tag{7}$$

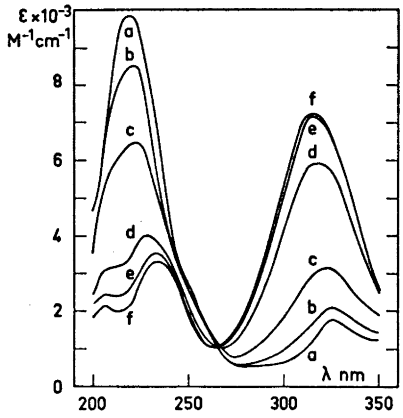

Fig. 5. ε data as a function of λ for rhodizonate solutions with different hydrogen ion concentrations. The following values for $-\log h$ were used: a. 4.77; b. 4.03; c. 3.67; d. 3.21; e. 3.02; f. 2.86.

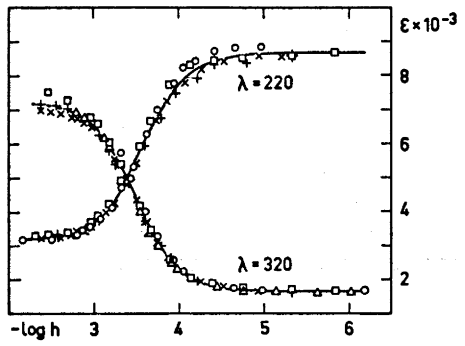

Fig. 6. The apparent molar absorptivity, ε, as a function of $-\log h$. The values for B are +0.8909 mM, ○ 0.7769 mM, □ 0.6615 mM, △ 0.5417 mM, and × 0.4553 mM. The curve drawn is $\varepsilon = f(h)$ (eqn. 7) with the "best" values for β_i and ε_p inserted.

Since ε can be calculated as a function $\varepsilon\ (\log h)_{B,\lambda}$ from eqn. (6), the values of the various molar absorptivities and stability constants can be deduced from eqn. (7). Starting from the preliminary values of β_1 and β_2 obtained in the emf work, the experimental spectrophotometric data were processed with the spectrophotometric version of the LETAGROP program.[25] The following "best values" for β_1 and β_2 were then obtained (*cf.* Fig. 6 and Table 3).

Table 3. Molar absorptivities, ε_p, at different wavelengths and stability constants, β_i obtained from the spectrophotometric data for rhodizonic acid. The errors are given as 3σ where σ is the standard deviation in ε_p and β_i, respectively.

λ (nm)	ε_0 (M^{-1} cm^{-1})	ε_1 (M^{-1} cm^{-1})	ε_2 (M^{-1}) cm^{-1})	log β_1	log β_2
220	8730 ± 130	3800 ± 1200	3190 ± 150	3.06 ± 0.46	7.03 ± 0.30
320	1670 ± 110	3200 ± 1100	7320 ± 150		

$$\log (\beta_1 \pm 3\sigma) = 3.06 \pm 0.46$$

$$\log (\beta_2 \pm 3\sigma) = 7.03 \pm 0.30$$

The error squares sum, U, defined as

$$U = \sum(\varepsilon_{calc} - \varepsilon)^2$$

was 3.67×10^6 for 144 values. According to the results obtained from the emf data, the actual B values for rhodizonic acid were only 90 % of the analytical ones. Calculations were therefore also performed with a total concentration $B' = 0.90B$. The "best values" obtained were then

$$\log (\beta_1 \pm 3\sigma) = 3.06 \pm 0.47$$

$$\log (\beta_2 \pm 3\sigma) = 7.03 \pm 0.30$$

and $U = 4.55 \times 10^6$ for 144 values. It is thus obvious that whereas a small adjustment of the total concentration, B, makes the fitting much better for the emf data (*cf.* Figs. 3 and 4) it does not influence the results obtained from the spectrophotometric data.

DISCUSSION

The acidity constants of squaric acid obtained in this work are in agreement with those hitherto reported (*cf.* Table 4), if differences in ionic strength are taken into consideration. The pK_{a2} value was determined with a higher precision than pK_{a1}, since the reaction $A^{2-} + H^+ \rightleftharpoons HA^-$ occurs at hydrogen ion

Table 4. Survey of reported values for the acidity constants of squaric acid.

	Method	Ionic strength (M)	Temp. °C	pK_{a1}	pK_{a2}
Park *et al.*[14]				–	3
Ireland and Walton [11]	Emf	0.1	25	≤ 1.7	3.21
MacDonald [13]	Emf	corr. to 0	25	1.2	3.48
Tedesco and Walton [12]	Emf	0.5	25	–	2.89
	Spectr.	1	25	0.40	–
This work	Emf	3	25	0.96	3.19

concentrations at which the emf methods are more accurate than they are in the region where the reaction $HA^- + H^+ \rightleftharpoons H_2A$ takes place (*cf.* Fig. 7).

The determination of the constants of rhodizonic acid was complicated by the instability of the acid and of its salts and it was consequently difficult to exclude decomposition products.

In the emf work the solutions were kept in a nitrogen atmosphere during all the measurements and no decomposition could be detected when pH > 2.7, not even after 24 h. It appears that the results obtained by this method are more accurate than those obtained spectrophotometrically, where the measurements were made after the solutions left the nitrogen atmosphere.

After the analytical concentrations, B, had been corrected in the emf data, the experimental points fitted well to the theoretical curve (*cf.* Fig. 4). The values obtained for the stability constants from the emf measurements ($\log \beta_1 = 3.58 \pm 0.05$ and $\log \beta_2 = 7.03 \pm 0.06$) therefore appear to be reliable and are, moreover, supported by the spectrophotometric measurements.

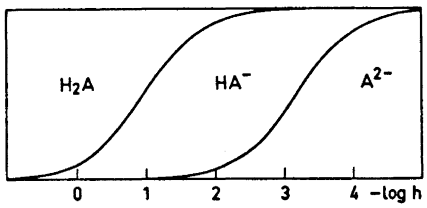

Fig. 7. The distribution of complexes as a function of $-\log h$ for squaric acid.

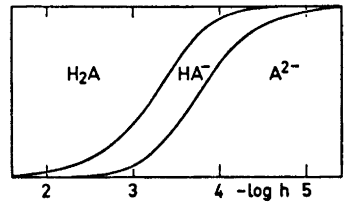

Fig. 8. The distribution of complexes as a function of $-\log h$ for rhodizonic acid.

The values reported earlier for the constants of rhodizonic acid differ considerably from those obtained in this work. Schwarzenbach and Suter [7] used emf and spectrophotometric methods in their investigations and studied oxidation-reduction potentials as functions of pH. Through their experimental points they drew straight lines and from the intersections of these lines they obtained pK_a values. For pH < 3 and pH > 6 the potentials are uncertain since the oxidation-reduction reactions are slow.

Table 5. Survey of reported values for the acidity constants of rhodizonic acid.

	Method	Ionic strength (M)	Temp. °C	pK_{a1}	pK_{a2}
Carpéni [5]	Emf	0.003	20	3.15	4.9
Schwarzenbach and Suter [7]	Emf		25		
	Spectr.		25	3.15	4.9
Preisler *et al.*[8]	Emf	0.1	30	4.1	4.5
Banerje *et al.*[10]	Emf	0.1	25	–	5.06
Takahashi *et al.*[9]	Spectr.			4.20	4.65
This work	Emf	3	25	3.45	3.58
	Spectr.	3	25	3.9	3.1

Preisler *et al.*[8] used the same method. As these authors later remarked [26] it is also possible to draw the lines in other ways and thus obtain other pK_a values, without impairing the goodness of fit to the experimental points.

In their spectrophotometric work, Schwarzenbach and Suter [7] used buffer solutions, carbonates, acetates, and malonates, to regulate the pH values. The solutions were saturated with carbon dioxide to prevent oxidation. The value obtained by this method ($pK_{a2} = 4.9$) is 1.3 units greater than that obtained in the present work. To investigate whether or not the discrepancy was reasonable, some preliminary spectrophotometric measurements were made with sodium rhodizonate dissolved in standard phosphate buffers with an ionic strength of about 0.1 M. We then obtained pK_a values that were approximately 1 unit higher than in 3 M $NaClO_4$. The differences between our pK_a values for rhodizonic acid and the more approximate values reported earlier [5–9] might therefore be due to an ionic strength effect.

In agreement with the molecular orbital calculations made by West and Powell [1] squaric acid has been found to be a stronger acid than rhodizonic acid and the anions of squaric acid are more stable than those of rhodizonic acid. Croconic acid (with an odd number of carbon atoms) is, however, according to the investigation made by Carlqvist and Dyrssen,[6] the strongest of the three acids ($pK_{a1} = 0.32$ and $pK_{a2} = 1.51$). This is in contradiction to the prediction that the strength of the acid should decrease with increasing ring size.[1]

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