

Summary

1. We have improved the Frankel and Cornelius method for preparing β -aminoethylsulfuric acid from monoethanolamine and sulfuric acid so that the theoretical yields may be obtained readily.
2. The crude product is purified easily, since water is the only other reaction product.
3. Although copiously soluble in water, the compound is not precipitated, even from its concentrated solutions, by acids, alkalies, or salts.
4. In aqueous solution the compound exists

in the simplest possible state of molecular aggregation.

5. The compound displays many of the properties common to the aliphatic amino acids.
6. The ester linkage of the compound is very resistant to hydrolysis, thus allowing it to be used in solution with substances that catalyze hydrolytic reactions.
7. The compound is worthy of further study as an ampholyte.

MADISON, WISCONSIN

RECEIVED JULY 7, 1938

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NEW YORK UNIVERSITY COLLEGE OF MEDICINE]

Complex Formation between Carboxylic Acids and Divalent Metal Cations

BY R. KEITH CANNAN AND ANDRE KIBRICK

This paper contains a comparison of the hydrogen electrode titration curves of a number of mono- and dicarboxylic acids in 0.2 *M* potassium chloride and in various KCl-MCl₂ solutions of the same ionic strength. *M* represents Mg, Ca, Sr, Ba or Zn. The work was instigated by recent observations of Greenwald¹ on the effect of calcium chloride on the *pH* of a variety of carboxylic acid buffer solutions. Its immediate purpose was to provide information as to the relative activity coefficients of certain salts of physiological importance but observations were extended to a number of related cations and acids. The ionic strength at which observations were made is comparable to that of mammalian body fluids.

The results indicate the existence of notable specific effects which are consistently related not only to the nature of the cation but to the molecular structure of the acid. These effects have been reduced to mass action constants for the formation of binary compounds between the carboxylate anions and each cation. Within the range of concentrations studied, and within the plausible errors of the method, we find that the formation of binary compounds suffices for a fairly satisfactory quantitative description of the observations. Were association to more complex compounds to occur to any important extent, we should expect the specific effects which have been observed to be a function of the total concentration of organic acid. We have found no

clear indication of this for concentrations of acid ranging from 0.002 to 0.05 *M* (Tables III and VII).

In our use of the law of mass action to describe the effects observed, we are committed to no particular views as to the nature of the forces involved. It is generally acknowledged that mass action constants may be expected to describe, with fair precision, certain specific electrostatic effects, whose existence is ignored in the approximations which are involved in the working equations of interionic attraction theory. Where electrostatic forces of ions are involved the definition of what constitutes a reversibly dissociable compound is difficult. The mass action constants are submitted merely as convenient descriptions of relative activity coefficients.

We appreciate the fact that the use of the hydrogen electrode introduces indeterminate errors due to the presence of a liquid junction (L. J.) potential. The observations comprise two types of hydrogen electrode potentials: (a) those of the organic acid buffer in KCl-MCl₂ solutions; and (b) those of dilute solutions of hydrochloric acid in corresponding KCl-MCl₂ solutions. The latter were employed to calculate γ_{H^+} for the corresponding solutions containing the carboxylic acid. Into both of these potential measurements L. J. potentials enter as a source of error. In the majority of the calculations, however, γ_{H^+} appears only as a small correction term. Its precise value is unimportant. In the few systems in which it is an important term (those of rather low

(1) I. Greenwald, *J. Biol. Chem.*, **124**, 437 (1938).

pH), the association constants derived with its aid are in satisfactory agreement with those calculated from observations at much higher pH , where its significance is small. Apart from the question of γ_{H^+} , indeterminate L. J. potentials enter into all the observations. We believe that the evidence is good that the method which we have adopted for the calibration of the reference electrode² eliminates the greater part of the potential at a broad junction between saturated potassium chloride and dilute electrolyte solutions containing few H^+ or OH^- ions. However this may be, our calculations depend, not upon the absolute potentials of any one solution, but upon changes in potential as MCl_2 is substituted for potassium chloride at constant ionic strength. The calculated association constants are based on changes in potential varying between 5 and 80 mv. The simultaneous changes in L. J. potentials must be very small compared with these. Using Henderson's equation to indicate their order of magnitude, we calculate differences, in extreme cases, of only 0.4 mv. It is fair to conclude that the calculated mass action constants provide a fairly satisfactory measure of relative activity coefficients.

Apart from the question of L. J. potentials, the calculations require the assumptions (a) that carboxylate anions do not associate to a significant extent with Na^+ or K^+ , (b) that in solutions containing MCl_2 , no significant concentration of MCl^+ exists. The former assumption conforms to prevailing views of the state of the alkali salts of organic acids in dilute solutions such as those used in this investigation. The absence of $CaCl^+$ and $BaCl^+$ receives support from the activity coefficients of calcium and barium chlorides published by Scatchard and Tefft.³ The observations of these authors on zinc chloride at $\mu = 0.20$ may be taken, however, to indicate significant concentrations of $ZnCl^+$ in our solutions. This we have ignored. The essential effect of the presence of this complex on the calculated constants would be to increase them all in the proportion $(Zn^{++}) + (ZnCl^+)/Zn^{++}$.

Experimental

Measured volumes of standard solutions of the acid and of sodium hydroxide were mixed. Amounts of M KCl and of $0.33 M$ MCl_2 were added to give the desired cation

(2) E. A. Guggenheim and T. D. Schindler, *J. Phys. Chem.*, **38**, 533 (1933).

(3) G. Scatchard and R. F. Tefft, *THIS JOURNAL*, **52**, 2272 (1930).

mixtures, and the whole was diluted to $\mu = 0.2$ (calculated from $KCl-MCl_2$ only). In this way the concentration of divalent cation was varied while approximate constancy of μ was maintained. The concentration of monocarboxylic acids was usually $0.02 M$ and of dicarboxylic acids $0.01 M$. The ionic strength would increase with the degree of neutralization and decrease with the extent of complex formation. For a $0.01 M$ dicarboxylic acid the range of μ under these influences would be 0.23 to 0.17. Actual calculations of μ for representative reaction systems, using the association constants found, showed that μ seldom fell outside of the range 0.19–0.21. It is improbable that activity coefficients would be seriously affected by such variation.

The pH of each reaction mixture was measured in a rocking hydrogen electrode (Clark) using a saturated calomel electrode and a saturated salt bridge. The reference electrode was calibrated by means of $0.1 M$ acetic acid– $0.1 M$ sodium acetate to which a pH of 4.66 was assigned.² The liquid junction potential was taken to be -2.4 mv. This was calculated from Henderson's equation.⁴ The potential of the junction, saturated potassium chloride–reaction mixture, was taken to be -1.3 mv. in all cases. Calculations for the junctions with $0.2 M$ potassium chloride and with $0.067 M$ magnesium, calcium or barium chlorides gave values varying from 1.1 to 1.5 mv.

A series of determinations were made of the pH of 0.01 and $0.002 M$ hydrochloric acid in salt mixtures representative of those used in the reaction mixtures. The values of $-\log \gamma_{H^+}$ calculated from these ranged from 0.090 to 0.110. Since the precise value of $[H^+]$ is important only in a few systems of low pH , we have been content to take $-\log \gamma_{H^+} = 0.100$ for all systems.

The recorded potentials were found immediately after preparation of reaction mixtures and were accurately reproducible over many hours. The reproducibility of the potential of duplicate reaction mixtures was about 0.2 mv.

Monocarboxylic Acids.—The following relations may be stated for an organic acid, HA , at a chosen ionic strength⁵

$$(a) (T_A) = (HA) + (A^-) + (MA^+)$$

$$(b) (T_m) = (M^{++}) + (MA^+)$$

$$(c) (Na^+) + (H^+) = (A^-) + (MA^+)$$

$$(d) K_1 = [H^+](A^-)/(HA)$$

$$(e) C_1 = (MA^+)/(A^-)(M^{++})$$

(T_A) , (T_m) and (Na^+) are known from the composition of the reaction mixtures. $[H^+]$ is calculated from $pH = -\log [H^+]$, and (H^+) is obtained with the aid of γ_{H^+} . In systems containing no MCl_2 , (A^-) is, then, calculated from (c), (HA) from (a) and K_1 from (d). In the presence of MCl_2 , (HA) is obtained from (a) – (c), (A^-) from (d), (MA^+) from (a) or (c), (M^{++}) from (b) and C_1 from (e).

(4) In this equation concentrations were employed in place of activities. The latest values for the transference numbers of potassium chloride were used [MacInnes and Dole, *THIS JOURNAL*, **53**, 1357 (1931)].

(5) Square brackets indicate activities and parentheses, concentrations.

In the special case where (T_m) is so much larger than (T_A) that we may put $(M^{++}) = (T_m)$, the dissociation curve of the acid suffers a parallel displacement on the pH ordinate from its position when MCl_2 is not present. The new curve will be that of an acid with an apparent dissociation constant

$$K_1' = \frac{[(A^-) + (MA^+)] [H^+]}{(HA)} = K_1 [C_1(T_m) + 1]$$

Dicarboxylic Acids.—The assumption of binary compound formation implies the formation of MA^+ from A^- and of MA from $A^{=}$. The pertinent relations are

$$(a') \quad (T_A) = (HA) + (A^-) + (A^{=}) + (MA^+) + (MA)$$

$$(b') \quad (T_m) = (M^{++}) + (MA^+) + (MA)$$

$$(c') \quad (Na^+) + (H^+) = (A^-) + 2(A^{=}) + (MA^+) + 2(MA)$$

$$(d') \quad K_1 = \frac{(A^-)[H^+]}{(HA)}$$

$$(e') \quad K_2 = \frac{(A^{=})[H^+]}{(A^-)}$$

$$(f') \quad C_1 = \frac{(MA^+)}{(A^-)(M^{++})}$$

$$(g') \quad C_2 = \frac{(MA)}{(A^{=})(M^{++})}$$

There are not sufficient equations for the calculation of either the dissociation or the association constants from a single observation. Under appropriately restricted conditions, however, we may make approximations to each of them in turn and then attempt to adjust the preliminary values so as to conform simultaneously to all observations. Provided the latter cover a sufficient range of (T_m) and a range of pH corresponding to a wide variation in $(A^-)/(A^{=})$, successive approximations to a pair of constants may be made with confidence. In the absence of MCl_2 , observations at low pH may be used to calculate a preliminary value for K_1 , since $(A^{=})$ will be very small. Corresponding observations at high pH will give an approximation to K_2 . These constants are then adjusted to observations at intermediate values of pH until the best fit is attained. This is the common practice in deriving dissociation constants of polyvalent acids or bases from their dissociation curves.

The same procedure may now be applied to determine C_1 and C_2 from observations on solutions containing MCl_2 , using the above values for K_1 and K_2 . Where $(T_m)/(T_A)$ is large, the curve will be that of a dicarboxylic acid with apparent constants $K_1' = K_1[C_1(T_m) + 1]$ and

$$K_2' = K_2 \frac{C_2(T_m) + 1}{C_1(T_m) + 1}$$

From observations at appropriate extremes of pH , preliminary values of K_1' and K_2' and, hence, of C_1 and C_2 may be obtained. In the refinement of the values of the latter, we have found it convenient to introduce the quantity

$$K_4 = \frac{(MA)[H^+]}{(MA)^+} = K_2 C_2 / C_1$$

and to impose the successive approximations on this. Combining equations (a') to (g') and introducing K_4 we have derived

$$\alpha = \frac{((Na^+) + [H^+]) / (T_A - x/w)}{(2K_4 + [H^+]) / (K_4 + [H^+]) - x/w} \quad (1)$$

and

$$C_2 = \frac{\alpha}{1 - \alpha} \cdot \frac{K_4 w}{K_1 K_2 (K_4 + [H^+])} \cdot \frac{1}{(T_m) - \alpha(T_A)} \quad (2)$$

where α is the fraction of the total acid combined with the cation

$$x = 2K_1 K_2 + K_1 [H^+]$$

and

$$w = K_1 K_2 + K_1 [H^+] + [H^+]^2$$

The preliminary values of C_1 and C_2 fix a tentative value for K_4 and this allows calculations of α and of C_2 from (1) and (2), respectively. K_4 is subjected to minor adjustments until consistent values for C_2 emerge from observations over the whole experimental range of (T_m) and of pH .

Results

Monocarboxylic Acids.—The results are so extensive that only a few representative experiments can be given in detail. In Table I the

TABLE I

	(Na ⁺) × 10 ³	ACETIC ACID, $T_A = 0.0200$					
		0.200 M KCl	0.0636 M ZnCl ₂	0.0664 M MgCl ₂	0.0668 M CaCl ₂	0.0670 M SrCl ₂	0.0662 M BaCl ₂
		pH					
A	6.264	...	4.096	4.212	4.219	4.237	4.240
B	8.352	4.496	4.280	4.413	4.401	4.421	4.430
C	10.44	4.675
D	12.53	4.864	4.663	4.782	4.780	4.797	4.800
E	14.62	5.076	4.876	4.990	4.993
F	16.70	5.347	5.149	5.262	5.265	5.260	5.279
G	18.79	5.842	...	5.761	5.761
		α					
A		0.123	0.061	0.058	0.046	0.045	
B		.168	.075	.085	.070	.058	
C		
D		.236	.112	.114	.090	.083	
E		.270	.133	.127	
F		.308	.150	.146	.140	.112	
G	138	.143	
		$K_1 \times 10^3$					
A		...	10.7	3.67	3.41	2.58	2.52
B		2.31	11.0	3.81	3.91	2.43	2.49
C		2.32
D		2.30	10.2	3.38	3.45	2.58	2.38
E		2.29	10.1	3.47	3.27
F		2.29	10.1	3.45	3.30	3.11	2.43
G		2.24	...	2.70	2.81
Mean		2.29	10.4	3.4	3.4	2.7	2.4
		Logarithm					
		-4.640	1.02	0.53	0.53	0.43	0.38

data of an experiment on acetic acid are recorded. Table II relates to a similar experiment with glycolic acid. These two tables illustrate the constancy of C_1 despite a 4- to 5-fold variation in anion concentration. The effect of MCl_2 on the unsubstituted acids was very small and the calculated values of C_1 are correspondingly irregular.

TABLE II

GLYCOLIC ACID, $T_a = 0.01996 M$							
	(Na^+) $\times 10^3$	0.200 M KCl	0.0636 M ZnCl ₂	0.0664 M MgCl ₂	0.0668 M CaCl ₂	0.0670 M SrCl ₂	0.0662 M BaCl ₂
pH							
A	4.176	3.231	2.671	3.090	3.019	3.105	3.134
B	8.352	3.598	2.948	3.425	3.359	3.457	3.493
C	12.53	3.949	3.275	3.775	3.708	3.809	3.845
D	16.70	4.428	3.748	4.256	4.190	4.289	4.320
α							
A		0.284	0.084	0.122	0.076	0.076	0.059
B		.402	.154	.200	.129	.129	.100
C		.537	.215	.284	.184	.184	.143
D		.683	.282	.363	.237	.237	.191
C_1							
A	$K_1 \times 10^4$	1.92	82.2	7.35	12.7	6.3	4.60
B		1.94	82.2	8.46	12.9	6.46	4.58
C		1.95	81.8	8.24	13.0	6.43	4.59
D		1.95	82.8	8.28	12.8	6.30	4.73
Mean		1.94	82.2	8.1	12.8	6.4	4.6
Loga- rithm		-3.712	1.91	0.91	1.11	0.81	0.66

TABLE III

GLYCOLIC ACID AND ACETIC ACID, EFFECT OF VARYING T_m AND T_a					
T_m	T_a	(Na ⁺) $\times 10^3$ pH Acetic acid—ZnCl ₂		α	Log C_1
0.0318	0.0200	12.53	4.753	0.145	1.02
		14.62	4.963	.168	1.02
		16.70	5.228	.204	1.06
.0636	.0500	10.44	3.856	.083	1.03
		20.88	4.284	.162	1.06
Glycolic acid—ZnCl ₂					
0.0636	0.00499	2.61	3.273	0.560	1.89
.0318			3.427	.419	1.85
.0191			3.538	.316	1.84
.0127			3.600	.267	1.87
.00636			3.700	.158	1.84
.0636	.02994	15.66	3.077	.455	1.95
	.01996	10.44	3.097	.470	1.92
	.00998	5.22	3.154	.504	1.89
	.00499	2.61	3.273	.560	1.89
Glycolic acid—CaCl ₂					
0.0668	0.00499	2.61	3.604	0.263	1.09
.0318			3.698	.161	1.08
.0191			3.745	.103	1.01
.0127			3.779	.058	0.94
.0668	.02994	15.66	3.516	.244	1.14
	.01996	10.44	3.527	.243	1.12
	.00998	5.22	3.557	.249	1.10

When T_m was reduced below 0.03 the displacements of pH were too small to justify calculations. With the hydroxy acids, on the other hand, a five-fold variation of T_m and T_a was possible (Table III). The variations in C_1 are well within the possible effects of the accompanying variations in μ and the liquid junction potentials. The constants for the eight monocarboxylic acids are assembled in Table IV.

TABLE IV

LOG C_1 FOR MONOCARBOXYLIC ACIDS ($\mu = \text{circa } 0.2$)						
Acid	Zn	Mg	Ca	Sr	Ba	pK_1
Acetic	1.03	0.51	0.53	0.43	0.39	4.640
Propionic	1.01	.54	.50	.43	.34	4.703
Butyric	1.00	.53	.51	.36	.31	4.742
β -Hydroxybutyric	1.06	.60	.60	.47	.43	4.390
Glycolic	1.92	.92	1.11	.80	.66	3.712
Lactic	1.86	.93	1.07	.70	.55	3.739
Glyceric	1.80	.86	1.18	.89	.80	3.517
Gluconic	1.70	.70	1.21	1.00	.95	3.556

Association Constants of Davies⁶ for CaA^+ ($\mu = 0$)

Acetic	0.0
β -Hydroxybutyric	.82
Glycolic	1.58
Lactic	1.47

The more significant conclusions are:

1. The three unsubstituted acids and the β -hydroxy acid give almost identical constants for a particular cation.

2. The constants of the four α -hydroxy acids are also very similar in magnitude but are much greater than those of the unsubstituted acids. A hydroxyl in other positions has little effect although the results with glyceric and gluconic acids suggest a slight enhancement of association with the alkaline earth cations and a slight depression with Zn^{++} and Mg^{++} .

3. The relative tendencies of the cations to associate with any one anion is in the order $Zn \gg Ca > Sr > Ba$. The position of Mg is irregular. In the series of the alkaline earth cations, the effect of the size of the cation is manifest. No simple relation is apparent between K_1 and C_1 but it is worthy of remark that the α -hydroxyl which so notably enhances association of the carboxylate ion with these divalent cations, as strongly reduces its association with the hydrogen ion.

In a very recent publication, Davies⁶ has reported the dissociation constants of a number of calcium carboxylates which he has calculated from conductivities or from solubility data. They refer to $\mu = 0$. The logarithms of their

(6) C. W. Davies, *J. Chem. Soc.*, 277 (1938).

reciprocals are included in Table IV. For comparison, our values must be increased by an activity coefficient term which will approximate $-\log \gamma_{\text{Ca}^{++}}$. If we assign to the latter the reasonable value of 0.35 at $\mu = 0.2$, we find fairly satisfactory agreement between the two sets of constants. The one exception is the case of acetic acid. When the constant is as small as it would appear to be with the unsubstituted acids, the calculations, both from conductivities and from potentiometric data, are very uncertain.

Dicarboxylic Acids.—The values derived for K_1 and K_2 of the various acids agree fairly well with values in the literature where comparisons on the basis of μ are possible. Their absolute magnitude is unimportant to our argument provided they define our data for potassium chloride systems with precision. This they do to the extent that, in no case, was the difference between (Na^+) , calculated from pH and x/w , and (Na^-) , derived from the composition of a mixture, greater than 0.005 equivalent. Details of the potassium chloride experiments are omitted.

The results for MCl_2 with one unsubstituted and with one hydroxy acid are illustrated in Tables V, VI and VII. The mean values of C_2 (as $\log C_2$) of the six dicarboxylic acids studied are assembled in Table VIII together with the values for $\text{p}K_4$ which finally were adopted and those of $\log C_1$ calculated from $\text{p}K_4$. In some cases the range of observations was limited by the insolubility of the particular complexes. With oxalic

TABLE VI
MALIC ACID $T_a = 0.009605$

	$(\text{Na}^+) \times 10^3$	0.0636	0.0664	0.0668	0.0670	0.0662
		$\frac{M}{\text{Zn}}$	$\frac{M}{\text{Mg}}$	$\frac{M}{\text{Ca}}$	$\frac{M}{\text{Sr}}$	$\frac{M}{\text{Ba}}$
		pH				
A	0	2.491	2.669	2.634	2.677	2.684
B	4.052	2.786	...	3.041
	4.176	...	3.121	...	3.126	3.143
C	8.241	3.119	...	3.500
	8.352	...	3.586	...	3.625	3.651
D	12.16	3.486	...	3.982
	12.53	...	4.097	...	4.161	4.212
E	16.48	4.037	4.699	4.640
	16.70	4.834	4.900
<hr/>						
A		0.290	0.086	0.128	0.078	0.067
B		.411	.130	.205	.132	.116
C		.591	.246	.352	.242	.215
D		.747	.400	.504	.404	.355
E		.912	.581	.685	.569	.496
<hr/>						
		$\text{Log } C_2$				
A		2.85	1.60	1.83	1.45	1.33
B		2.82	1.54	1.75	1.39	1.25
C		2.84	1.57	1.79	1.40	1.29
D		2.85	1.58	1.80	1.48	1.35
E		2.97	1.60	1.82	1.51	1.36

TABLE VII
MALONIC ACID, EFFECT OF VARYING T_a AND T_m

T_m	T_a	$(\text{Na}^+) \times 10^3$	pH	α	$\text{Log } C_2$
ZnCl₂					
0.0654	0.01	16.70	4.105	0.739	2.83
.0327		16.70	4.430	.666	2.74
.01308		8.352	3.325	.094	2.74
.01308		12.53	4.093	.267	2.70
.01308		16.70	4.832	.562	2.78
MgCl₂					
0.0664	0.01	16.70	4.829	0.623	1.96
.0332	.01	16.70	5.079	.487	1.89
.01328	.01	16.70	5.336	.269	1.78
.00664	.01	16.70	5.438	.164	1.90
.0664	.05	20.62	2.581	.060	1.78
		41.25	3.225	.127	1.84
		61.87	4.151	.298	1.90
		82.50	4.936	.521	1.91
CaCl₂					
0.0664	0.01	16.70	5.154	0.504	1.52
.0332			5.326	.333	1.45
.01336			5.451	.165	1.43
SrCl₂					
0.0670	0.01	16.70	5.284	0.407	1.27
.0335			5.406	.248	1.21
.0134			5.489	.117	1.17
BaCl₂					
0.0662	0.01	16.70	5.294	0.412	1.27
.0331			5.409	.247	1.21
.01324			5.492	.109	1.16

TABLE V
MALONIC ACID $T_a = 0.01$

	$(\text{Na}^+) \times 10^3$	Zn	Mg	Ca	Sr	Ba
		0.0636	0.0664	0.0668	0.0670	0.0662
		pH				
A	0	2.436	2.464	2.473	2.476	2.471
B	4.176	2.723	2.798	2.809	2.809	2.813
C	8.352	3.085	3.319	3.393	3.403	3.401
D	12.532	3.540	4.122	4.415	4.540	4.541
E	16.700	4.105	4.829	5.154	5.284	5.294
<hr/>						
		α				
A		0.125	0.072	0.071	0.063	0.076
B		.174	.101	.094	.093	.085
C		.284	.178	.130	.134	.147
D		.470	.353	.303	.240	.256
E		.739	.623	.504	.407	.412
<hr/>						
		$\text{Log } C_1$				
A		2.85	1.92	1.48	1.26	1.31
B		2.79	1.88	1.43	1.16	1.18
C		2.80	1.94	1.41	1.25	1.26
D		2.80	1.93	1.51	1.24	1.26
E		2.83	1.96	1.52	1.27	1.27

TABLE VIII
 DICARBOXYLIC ACIDS—SUMMARY OF RESULTS

Acid	pK_1	pK_2	Log C_2						Mg (Simms) $\mu = 0.07$
			Zn	Mg	Ca	Sr	Ba		
Oxalic	1.14 ?	3.85		2.55					2.65
Malonic	2.69	5.24	2.78	1.91	1.46	1.25	1.23		2.06
Succinic	4.07	5.28	1.78	1.20	1.20	1.06	1.03		0.98
Glutaric	4.21	5.06	1.60	1.08	1.06
Azelaic	4.40	5.1572
Malic	3.26	4.68	2.80	1.55	1.80	1.45	1.30		...
r-Tartaric	2.88	3.94	2.68	1.36	1.80	1.65	1.62		...
Oxalic Acid (Money and Davies ⁹) $\mu = 0$			4.89	3.43	3.00	2.54	2.33		

	pK_4					Log C_1				
	Zn	Mg	Ca	Sr	Ba	Zn	Mg	Ca	Sr	Ba
Oxalic		1.8 ?					0.5 ?			
Malonic	3.3	3.8	4.25	4.4	4.45	0.84	.47	0.47	0.41	0.44
Succinic	4.4	4.6	4.6	4.7	4.7	.90	.52	.52	.48	.45
Glutaric	4.3	4.5	4.584	.52	.50
Malic	3.45	3.9	3.9	3.95	4.0	1.57	.77	1.02	.72	.67
r-Tartaric	2.7	3.5	3.25	3.2	3.2	1.44	.92	1.11	.91	.88

acid, observations with Mg^{++} alone were possible. With tartaric acid and Ca^{++} they were limited to $T_m = 0.013$ or less. In a few other systems, a salt separated some hours after completion of observation. In these cases, the possibility of anomalous potentials due to precipitation at the electrode must be entertained. We have accepted potential observations only when they were stable for five minutes after cessation of rocking and only if they were reproducible after renewed rocking.

The values of K_4 and C_1 for oxalic acid are highly tentative because it was not possible to make accurate calculations from observations at the low pH range in which C_1 dominates the extent of association. The recorded value of C_2 for oxalic acid is, however, independent of K_4 , provided (as seems most probable) the latter is not much greater than 2. In general, there is less satisfactory agreement between individual values of C_2 for dibasic acids than was found for C_1 with the monobasic acids. This is inherent in the calculation which makes C_1 and C_2 very sensitive to the precise values of K_1 , K_2 and K_4 . We have not attempted to approximate pK_4 more closely than 0.05.

The following conclusions are submitted:

1. The unsubstituted dicarboxylic acids give values for C_1 very close to those of the unsubstituted monocarboxylic acids; *i. e.*, a COOH group is without important influence on association at a neighboring carboxylate ion.

2. Similarly, the hydroxy dicarboxylic acids give values for C_1 close to those of α -hydroxy monocarboxylic acids.

3. C_2 for a particular cation diminishes, first rapidly and then slowly, with increasing separation of the carboxyl groups in the dianion.

4. C_2 is increased as greatly by a single α -hydroxyl group as by two.

5. The cation series $Zn \gg Ca > Sr > Ba$ is found for C_2 , Mg being, again, irregular in position.

6. For a particular anion, C_2 is always much greater than C_1 , but no simple relation obtains. If complex formation actually involves the formation of a coordinate link, then the question of ring strain enters. Possibly the relative values of C_2/C_1 for a series of anions and a particular cation reflect this factor.

The values found for C_1 are small compared with C_2 . It may seem a precarious undertaking to attempt their evaluation from systems in which C_2 also operates. To ignore C_1 , however, is to ignore the behavior of the monocarboxylic acids. Without it, constant values for C_2 are not obtained. For example, in a series of malonic acid-zinc chloride mixtures quoted in Table V, the values of $\log C_2$ were 2.85, 2.79, 2.80, 2.80, 2.83. The corresponding values, when C_1 is assumed to be very small, are 3.26, 3.00, 2.82, 2.72, 2.62.

Simms⁷ has reported extensive potentiometric data on the titration of various acids in magnesium chloride solutions. Greenwald⁸ recently has shown that the specific effects observed may be reduced to mass action constants comparable

(7) H. S. Simms, *J. Phys. Chem.*, **32**, 1121 (1928).

(8) I. Greenwald, *ibid.*, in press (1938).

(9) R. W. Money and C. W. Davies, *Trans. Faraday Soc.*, **28**, 609 (1932).

with our C_2 . Greenwald's constants for oxalic acid and malonic acid are included in the last column of Table VIII together with those which we have calculated from Simms' observations on succinic and azelaic acids. For these calculations we used the method of the present paper. Simms' constants must be reduced slightly to translate them from $\mu = 0.07$ to 0.20. The activity correction is $-\log \gamma_{Ca^{2+}} \gamma_{A^{2-}}$. A reduction of $\log C_2$ by 0.1 is entirely reasonable. If that is done, the agreement is good, except for succinic acid.

Money and Davies¹⁰ have determined constants for oxalic acid and a series of cations from the conductivities of the salts (Table VIII). To convert these to $\mu = 0.2$ a reduction of $\log C_2$ by 0.6 – 0.8 is consistent with available data on the ac-

tivity coefficients of divalent ions. Agreement with our value for oxalic–Mg is then good and the relative behavior of the series of cations is in harmony with our observations on the other acids.

Summary

1. The hydrogen electrode titration curves of a number of mono- and bivalent carboxylic acids have been compared in varying KCl–MCl₂ mixtures of constant ionic strength ($\mu = 0.2$). (M represents Mg, Ca, Sr, Ba or Mg.)

2. The specific effects which have been observed have been reduced to mass action constants for the formation of binary compounds between the cations and the carboxylate anions.

NEW YORK, N. Y.

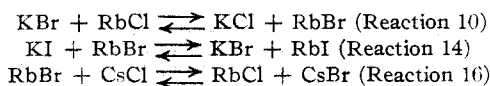
RECEIVED JUNE 8, 1938

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, ST. LOUIS UNIVERSITY SCHOOL OF MEDICINE]

A Study of Some Reactions between Dry Inorganic Salts. IV. Reactions below the Fusion Point¹

BY HAROLD L. LINK AND LYMAN J. WOOD

Recently all of the possible reactions that might occur between dry alkali halides above the fusion temperature have been studied by Thomas and Wood.² Of the possible 60 reactions that might occur between pairs of alkali halides not having a common ion, it was found that 57 of the reactions proceeded (in the fused state) to completion in such a direction that the average cube edge of the stable pair was less than the average cube edge of the reciprocal pair. In these 57 cases, without exception, the larger cation united with the larger anion and the smaller cation with the smaller anion. In each of these 57 cases, also without exception, the sum of the heats of formation of the stable pair was greater than that of the reciprocal pair, *i. e.*, ΔH was minus. In the remaining three cases equilibrium was indicated as represented in the following reactions



(1) Read at the Rochester meeting of the American Chemical Society, September, 1937. This communication is for the most part from a thesis presented by H. L. Link for the degree of Master of Science.

(2) (a) E. B. Thomas and Lyman J. Wood, *THIS JOURNAL*, **56**, 92 (1934); (b) *ibid.*, **57**, 822 (1935); (c) *ibid.*, **58**, 1341 (1936).

The present report concerns studies of reactions that have been made under the fusion point and is limited to double decompositions involving only Na⁺, K⁺, Rb⁺, Cs⁺, Cl⁻, Br⁻, and I⁻ (see reactions 1–18, Table I). The variation of the speed of reaction with time at a fixed temperature has been studied and also the variation of the speed with temperature for a fixed time. In five cases what appear to be equilibrium mixtures have been obtained and these mixtures have been studied in some detail.

Materials and Experimental Procedure

The salts used were Analytical Reagents with the exception of cesium chloride and bromide, which were prepared from the nitrate according to the method of Wells.³ The salts were fused and ground to a fine powder and kept in a desiccator until wanted. After heating the various salt pairs at temperatures and for lengths of time indicated in the proper place, all mixtures were examined by the method of X-ray crystal analysis as previously described.^{2a}

It is, in general, more difficult to obtain good films from salt mixtures which have been heated under the fusion point rather than above the

(3) H. L. Wells, *Am. J. Sci.*, [3] **46**, 186 (1893).