523. *Reaction-kinetic Investigations of the Incomplete Dissociation of Salts. Part III.* The Decomposition of Nitramide in Solutions of Some Metal Salts of Carboxylic Acids.*

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A kinetic study has been made of the decomposition of nitramide at 25° catalysed by the anions of five carboxylic acids, present in buffer solutions as the sodium, calcium, barium, or zinc salts. Values for the catalytic constants of the anions were calculated from the results for the sodium salts and closely obeyed the Brönsted relation. The reaction is specifically retarded by calcium, barium, and zinc ions. This retardation can be accounted for in terms of the partial formation of species such as $C_6H_5 \cdot CH(OH) \cdot CO_2Ca^+$ and $[O_2C \cdot CH_2 \cdot CH(OH) \cdot CO_2]Ca$. The values found for the dissociation constants of these species follow the same order as those previously obtained by other methods, but are uniformly somewhat higher. The discrepancy can be accounted for by assuming that the ions do not entirely lose their catalytic power when associated with a metallic cation, or by the equivalent assumption that the transition state in the reaction associates to some extent with these cations.

IN the previous papers of this series (Bell and Prue, *J.*, 1949, 362; Bell and Waind, *J.*, 1950, 1979) it was shown that, when bivalent metallic cations exert specific negative salt effects in reactions involving hydroxyl ions, these effects can be accounted for quantitatively in terms of incomplete dissociation of the metallic hydroxides. The values of the dissociation constants of species such as $CaOH^+$ were in fair agreement with those obtained from other sources. The same cations were found to have no specific retarding effect in certain reactions, and this was interpreted in terms of the properties of the transition state. The present work extends this kinetic method of investigating incomplete dissociation by measurements of the rate of decomposition of nitramide, catalysed by the anions of acetic, mandelic, salicylic, malic, and fumaric acids in the presence of sodium, calcium, barium, and zinc ions.

EXPERIMENTAL.

Nitramide was prepared by the method of Marlies, LaMer, and Greenspan (*Inorg. Synth.*, **1**, 68, 193) as white leaflets and was stored in a stoppered bottle in a desiccator.

The reactions mixtures were prepared from buffer solutions of sodium hydroxide and acid, to which was added a solution of sodium chloride, calcium chloride, barium chloride, or zinc perchlorate. The ionic strengths of the final solutions were adjusted to approx. 0·1 or 0·2 by the addition of sodium chloride solution (except for the zinc salts, for which sodium perchlorate solution was used). The pH of the buffer solutions was kept below 5, so that the catalytic effect of the nitramide ions could be neglected.

The sodium hydroxide solution was free from carbon dioxide and was standardised against constant-boiling hydrochloric acid. Acetic acid was " AnalaR " glacial, and other acids were estimated to be 99·9% pure by titration. The solutions of sodium chloride and sodium perchlorate were prepared by weight from " AnalaR " materials. The calcium and barium solutions were prepared from $BaCl_2,2H_2O$ (" AnalaR ") and calcium chloride (" AnalaR dried "). They were standardised by gravimetric chloride determinations, and also by determining barium as sulphate and calcium as oxalate (permanganate titration). The zinc perchlorate solution was prepared by treating standard perchloric acid solution with an excess of zinc oxide. All solutions were made up with distilled water free from carbon dioxide.

The kinetic measurements were carried out with the apparatus described by Bell and Caldin (*Trans. Faraday Soc.*, 1951, **47**, 50 : cf. also Bell and Trotman-Dickenson, *J.*, 1949, 1291). It had a total volume of about 20 c.c. and required only 4 c.c. of solution and 3 mg. of nitramide. The temperature was throughout 25° ± 0·01°. The reactions were always strictly of the first order, and velocity constants were calculated by Guggenheim's method (*Phil. Mag.*, 1926, **7**, 538).

RESULTS.

Table I gives the data for the sodium salts of the monobasic acids, together with the catalytic constants of the anions (k_b). The last were obtained by deducting from the observed velocity constant k ($\log_{10}$, min.$^{-1}$) the water velocity k_0 (taken throughout as 123×10^{-5}), and then dividing by the corrected anion concentration c. The latter was calculated from the stoicheiometric buffer composition and the

* Part II, *J.*, 1950, 1979.

thermodynamic dissociation constant of the acid, the hydroxyl-ion concentration being neglected. Activity coefficients were calculated from the equation given by Guggenheim (*Phil. Mag.*, 1935, **19**, 588) :

$$-\log_{10} f_z = 0.5 z^2 I^{\frac{1}{2}}/(1 + I^{\frac{1}{2}}) \qquad \qquad (1)$$

where z is the valency of the ion and I the ionic strength. All concentrations are given in moles/l., and a and b denote respectively the stoicheiometric concentrations of acid and of sodium hydroxide. The solutions were made up to the stated ionic strength by the addition of sodium chloride.

TABLE I.

10^4a.	10^5b.	10^5c.	10^5k.	k_b.	I.	10^4a.	10^4b.	10^4c.	10^5k.	k_b.	I.
		Sodium acetate.						Sodium mandelate.			
378	309	319	590	1·480	0·2	682	234	237	501	0·159	0·2
378 *	309	319	597	1·483	0·2	370	234	239	513	0·161	0·1
252	613	617	1036	1·481	0·2	732	467	470	860	0·157	0·2
252 *	613	617	1045	1·485	0·2	980	593	595	1020	0·154	0·1
			Mean	1·482					Mean	0·157	

10^4a.	10^4b.	10^4c.	10^5k.	k_b.	I.
		Sodium salicylate.			
365	310	310	320	0·0657	0·2
553	496	496	460	0·0670	0·2
677	814	814	660	0·0660	0·2
			Mean	0·0663	

* These solutions contained, in addition, 0·0398M-CaCl$_2$.

Table II gives the results for the sodium salts of the dibasic acids. The catalytic constants of the singly charged anions (k_b') and of the doubly charged anions (k_b'') were obtained by combining the results of experiments in which the buffer ratio was varied over as wide a range as possible (subject to keeping pH less than 5). The true composition of each buffer solution was calculated by successive approximations from the following set of equations :

$$2[A^{--}] = b + [H^+] - [HA^-]$$
$$\log_{10} [H_2A] = \log_{10} [H^+] + \log_{10} [HA^-] - \log_{10} K_1 - f(I)$$
$$[HA^-] = a - [A^{--}] - [H_2A]$$
$$\log_{10} [H^+] = \log_{10} K_2 - \log_{10} [A^{--}] + \log_{10} [HA^-] + 2f(I)$$

in which a = total acid concentration (stoicheiometric), b = sodium hydroxide concentration (stoicheiometric), H_2A, HA^-, A^{--} = acid molecule, singly charged anion and doubly charged anion respectively, K_1, K_2 = first and second thermodynamic dissociation constants of the acid, and $f(I)$ = $I^{\frac{1}{2}}/(1 + I^{\frac{1}{2}})$. The final results of the successive approximations are given in the Table. They should be related to the observed velocity by the equation $k = k_0 + k_b'[HA^-] + k_b''[A^{--}]$, and the best values for k_b' and k_b'' for a given acid were obtained by plotting $(k - k_0)/[HA^-]$ against $[A^{--}]/[HA^-]$. They are given before the results for each acid, and colum 4 of the table gives the velocity constants calculated from these values.

TABLE II.

10^4a.	10^4b.	10^4k, obs.	calc.	$10^4[H_2A]$.	$10^4[HA^-]$.	$10^4[A^{--}]$.	$10^4[H^+]$.	I.
		Sodium fumarate.	$k_b' = 0.113, k_b'' = 0.687$.					
243	333	100	98	12·1	127	104	1·7	0·126
333	408	104	108	29·6	196	108	2·9	0·164
473	534	127	131	60·5	288	125	4·3	0·239
357	533	155	159	10·8	159	188	1·2	0·147
316	509	167	162	4·9	112	199	0·8	0·171
		Sodium malate.	$k_b' = 0.270, k_b'' = 1.75$.					
379	371	171	180	61·8	263	55·0	1·62	0·174
512	459	205	207	108·4	347	57·5	2·25	0·212
526 *	459	210	202	117·4	355	53·4	2·28	0·175
427	459	239	240	50·7	291	85·3	2·09	0·211
395 *	574	396	397	9·2	195	190	0·34	0·187
512	735	489	497	14·8	262	237	0·41	0·200

* In these solutions the ionic strength was adjusted with sodium perchlorate instead of with sodium chloride.

The experimental results for solutions containing bivalent metallic cations are given in Table III.

TABLE III.

10^4a.	10^4b.	$10^4[CaCl_2]$.	10^5k.	10^4a.	10^4b.	$10^4[BaCl_2]$.	10^5k.
	Calcium mandelate.				Barium mandelate.		
412	239	546	423	850	213 †	570	737
467	234	252	442	765	426	237	760
711	478	496	750	1081	536	298	900
1093	598	141	980				
397	111 *	—	445		Barium salicylate.		
				71	860	445	813
	Calcium salicylate.				Barium malate.		
451	408	506	290				
399	336	492	340	526	459	287	1950
653	598	425	510	351	459	287	2280
				395	574	718	3180
	Calcium malate.				Zinc malate.		
408	399	687	1360			$10^4[Zn(ClO_4)_2]$.	
526	495	532	1440	127	239	290	595
427	459	266	1950	288	232	89	710
395	577	266	3110	422	558	184	1851
512	735	372	3440	422	536	115	2200
	Calcium fumarate.				Zinc mandelate.		
318	343	443	791	788	223	184	372
473	534	665	1210	656	294	92	504
453	710	177	1990	985	357	69	626
473	763	532	2165	985	357	69	630

* $b = [Ca(OH)_2]$. † $b = [Ba(OH)_2]$.

DISCUSSION.

The third column of Table IV contains the catalytic constants derived from the experiments with sodium salts (cf. Tables I and II). The two figures in parentheses are from the measurements by Baughan and Bell (*Proc. Roy. Soc.*, 1937, A, **158**, 464); the agreement is excellent.

TABLE IV.

Anion.	K_{HB}.	k_b (obs.).	k_b (calc.).
Salicylate	1.06×10^{-3}	0·0662 (0·0665)	0·0663
Hydrogen fumarate	9.6×10^{-4}	0·113	0·120
Mandelate	3.88×10^{-4}	0·157	0·142
Hydrogen malate	3.5×10^{-4}	0·270	0·265
Fumarate	4.1×10^{-5}	0·687	0·924
Acetate	1.75×10^{-5}	1·48 (1·48)	1·49
Malate	9.0×10^{-6}	1·75	2·92

The last column of Table IV contains the values of k_b calculated from the expression

$$k_b/q = 3.12 \times 10^{-4} \, (p/qK_{HB})^{0.758}$$

where K_{HB} is the thermodynamic dissociation constant of the acid conjugate to the catalysing anion, p is the number of equivalent protons in this acid, and q the number of equivalent points in the anion at which a proton can be attached. This the expression which Baughan and Bell (*loc. cit.*) found to hold for eight singly charged anions, and it agrees well with experiment for the singly charged anions in Table IV. The two doubly charged anions give values of k_b somewhat lower than predicted by the above expressions : this agrees with the original findings by Brönsted and Pedersen at 15°, and is also in agreement with Pedersen's theoretical prediction about the effect of charge (Brönsted and Pedersen, *Z. physikal. Chem.*, 1923, **108**, 185; Pedersen, *J. Phys. Chem.*, 1934, **38**, 581).

Table I shows that the addition of calcium ions to an acetate solution has no effect on its catalytic power, in agreement with the view that calcium acetate is almost completely dissociated. On the other hand, all the values of k in Table III are smaller than those calculated from the stoicheiometric anion concentrations and the catalytic constants given in Table IV. The following procedure was adopted to find out whether this reduction could be consistently

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interpreted in terms of the removal of a fraction of the anions by association with metallic cations.

In the experiments with monobasic acids (mandelic and salicylic) the concentration of free anions $[A^-]$ was taken as $(k - k_0)/k_b$, where k_b is the catalytic constant of the anion derived from experiments with sodium salts (cf. Table I). This is equivalent to assuming that the association product MA^+ exerts no catalytic effect. The value of $[A^-]$ was then combined with the stoicheiometric composition of the solution to give $[MA^+]$ and $[M^{++}]$, taking into account the change of $[H^+]$ produced by displacement of the buffer ratio. The concentration dissociation constant $K_c = [A^-][M^{++}]/[MA^+]$ was converted into the thermodynamic constant K_d by using activity coefficients given by equation (1). In interpreting the results for malic acid it is necessary to take into account the two equilibria defined by $K_c' = [HA^-][M^{++}]/[MHA^+]$, $K_c'' = [A^{--}][M^{++}]/[MA]$, with the corresponding thermodynamic constants K_d' and K_d''. It is not possible to derive both these constants directly from the experimental results, and the procedure adopted was to select by trial and error the value of K_d' which gave the best constancy in K_d''. As a first approximation K_d' was put equal to K_d for the mandelate of the same cation, since there is evidence (Davies, *J.*, 1938, 277) that the anions of a number of different α-hydroxy-acids associate to about the same extent with a given cation. For a given value of K_d' it was then possible to calculate the composition of each solution and the corresponding value of K_d''. This was done by successive approximations from the following set of equations, in which s is the concentration of added salt $[CaCl_2, BaCl_2, \text{ or } Zn(ClO_4)_2]$, and the other symbols have been previously defined :

$$[A^{--}] = (k - k_0 - k_b'[HA^-])/k_b''$$

$$\log_{10} [H^+] = \log_{10} K_2 + \log_{10} [HA^-] - \log_{10} [A^{--}] + 2f(I)$$

$$\log_{10} [H_2A] = \log_{10} [H^+] + \log_{10} [HA^-] - \log_{10} K_1 - f(I)$$

$$\log_{10} [MHA^+] = \log_{10} [M^{++}] + \log_{10} [HA^-] - \log_{10} K_d' + 2f(I)$$

$$[MHA^+] + 2[M^{++}] = [HA^-] + 2s + 2[A^{--}] - b - [H^+]$$

$$[MA] = s - [MHA^+] - [M^{++}]$$

$$[HA^-] = a - [MHA^+] - [MA] - [A^{--}] - [H_2A]$$

$$K_c'' = [M^{++}][A^{--}]/[MA]$$

$$\log_{10} K_d'' = \log_{10} K_c'' - 4f(I)$$

The values finally obtained for the malates are given in Table V. A large proportion of the observed catalysis is due to the doubly charged anion, and the effect of added cations is chiefly to remove this ion. For this reason the values of K_d' are uncertain, but the values of K_d'' are little affected by this uncertainty. The same method of treatment is applicable in principle to the results for fumaric acid, but here the association with cations is much smaller and the observed velocities can be accounted for by assuming that only one type of association, $M^{++} + A^{--} \rightleftharpoons MA$, is present. The corresponding values of K_d'' are given in Table V.

The mean values of the dissociation constants obtained are collected in Table VI. Our results can be compared with data from two other sources. Cannan and Kibrick (*J. Amer. Chem. Soc.*, 1938, **60**, 2314) give concentration dissociation constants for the metallic salts of many organic acids, including malic acid. These were obtained by observing the change of pH produced when salt solutions (*e.g.*, $CaCl_2$, $BaCl_2$, or $ZnCl_2$) are added to dilute buffer solutions at an ionic strength of about 0·2. Davies (*J.*, 1938, 276; 1939, 349; and other papers) has given thermodynamic dissociation constants for several of the salts we have studied, derived from solubility measurements at ionic strengths below 0·07. The values of K_d depend to some extent on the equation employed for ionic activity coefficients. To facilitate comparison with Davies's values we have recalculated K_d values from the K_c values in the present paper and from those given by Cannan and Kibrick using Davies's expression

$$-\log_{10} f_z = 0{\cdot}5z^2 \left\{ \frac{I^{\frac{1}{2}}}{1 + I^{\frac{1}{2}}} - 0{\cdot}2I \right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

in place of equation (1). The comparison of the different values is shown in Table VII. This shows clearly that all the values obtained by the kinetic method are higher than those obtained by other methods. Incorrect allowance for ionic activity coefficients might account for the difference between values derived from measurements at $I \sim 0{\cdot}2$ and those of Davies, but

TABLE V.

(The order of experiments is the same as in Table III.)

$10^4[A^-]$.	$10^4[CaA^+]$.	$10^4[Ca^{++}]$.	I.	K_c.	K_d.
Calcium mandelate.					
191	54	492	0·178	0·173	0·045
203	35	218	0·091	0·128	0·043
399	83	413	0·200	0·199	0·048
556	48	93	0·089	0·117	0·041
211	15	96	0·097	0·138	0·046
				Mean	0·044
Calcium salicylate.					
399	9·7	496	0·200	1·63	0·39
327	9·1	483	0·200	1·41	0·34
587	11·1	414	0·200	1·61	0·38
				Mean	0·37

$10^4[HA^-]$.	$10^4[A^{--}]$.	$10^4[Ca^{++}]$.	$10^4[CaA]$.	$10^4[CaHA^+]$.	I.	K_c''.	K_d''.
Calcium malate ($K_d' = 0.060$).							
221	37	608	29	50	0·232	0·078	0·0040
282	32	436	21	75	0·186	0·067	0·0042
263	64	218	22	26	2·160	0·063	0·0045
173	144	200	50	17	0·133	0·058	0·0049
230	154	260	86	26	0·170	0·047	0·0032
						Mean	0·0042
Calcium fumarate.							
193	66	431	12	—	0·171	0·24	0·016
280	112	648	17	—	0·259	0·42	0·019
193	240	159	19	—	0·142	0·20	0·016
164	270	502	30	—	0·254	0·45	0·021
						Mean	0·018

$10^4[A^-]$.	$10^4[BaA^+]$.	$10^4[Ba^{++}]$.			I.	K_c.	K_d.
Barium mandelate.							
387	40	743	—	—	0·198	0·36	0·25
404	20	216	—	—	0·099	0·40	0·15
506	30	269	—	—	0·101	0·40	0·16
						Mean	0·20
Barium salicylate.							
845	15	430	—	—	0·200	2·3	0·55

$10^4[HA^-]$.	$10^4[A^{--}]$.	$10^4[Ba^{++}]$.	$10^4[BaA]$.	$10^4[BaHA^+]$.	I.	K_c''.	K_d''.
Barium malate ($K_d' = 0.17$).							
338	52	272	4·6	11	0·162	0·31	0·014
192	114	250	13	14	0·223	0·22	0·011
177	147	659	44	14	0·271	0·22	0·009
						Mean	0·011

$10^4[A^-]$.	$10^4[ZnA^+]$.	$10^4[Zn^{++}]$.	I.	K_c.	K_d.
Zinc mandelate.					
159	87	98	0·078	0·018	0·0066
243	60	32	0·098	0·013	0·0041
320	48	21	0·137	0·014	0·0041
323	49	21	0·177	0·014	0·0035
				Mean	0·0045

$10^4[HA^-]$.	$10^4[A^{--}]$.	$10^4[Zn^{++}]$.	$10^4[ZnA]$.	$10^4[ZnHA^+]$.	I.	K_c''.	K_d''.
Zinc malate ($K_d' = 0.0060$).							
150	10	39	17	33	0·104	0·0025	0·00027
7	26	197	87	6	0·136	0·0058	0·00051
59	33	60	38	25	0·147	0·0052	0·00041
192	69	49	94	41	0·171	0·0036	0·00025
222	85	29	60	26	0·198	0·0041	0·00024
						Mean	0·00034

cannot explain discrepancies between measurements at comparable ionic strengths. Scatchard and Teft's data (*J. Amer. Chem. Soc.*, 1930, **52**, 2272) show that the zinc chloride solutions used by Cannan and Kibrick contained significant concentrations of $ZnCl^+$, which would cause their constant for zinc malate to be too low. However, this explanation does not apply for the calcium and barium salts.

It seems likely, therefore, that in the present reaction the decrease of velocity caused by the addition of bivalent cations is somewhat smaller than the decrease of anion concentration due to association. This state of affairs will arise if the metallic cations associate to some extent with the transition state of the reaction, though to a smaller degree than with the free anions. An alternative way of expressing the same fact is to state that the associated anions possess a catalytic power which is appreciable, though smaller than that of the free anions. Previous papers in this series have revealed two extreme types of behaviour in the effect of

TABLE VI.

Collected values.

	K_d'.			K_d''.		
	Ca.	Ba.	Zn.	Ca.	Ba.	Zn.
Mandelates	0·044	0·20	0·0045	—	—	—
Salicylates	0·37	0·55	—	—	—	—
Malates	0·06	0·17	0·006	0·0042	0·011	0·00034
Fumarates	—	—	—	0·018	—	—

TABLE VII.

C = Cannan and Kibrick's values (recalculated).
D = Davies's values.
K = Kinetic values, recalculated by using equation (2).

		Calcium.			Barium.			Zinc.		
		C.	D.	K.	C.	D.	K.	C.	D.	K.
Mandelates	K_d	—	0·035	0·051	—	0·17	0·20	—	—	0·0055
Salicylates	K_d	—	0·26	0·44	—	—	0·62	—	—	—
Acetates	K_d	0·6	1	>2	—	—	—	—	—	—
Malates	K_d'	0·03	—	0·08	0·14	—	0·22	0·011	—	0·010
	K_d''	0·0013	0·0022	0·0058	0·0030	0·0064	0·015	0·00020	—	0·00048
Fumarates	K_d''	—	0·010	0·025	—	—	—	—	—	—

association on the reactivity of the hydroxyl ion. In the first (found in the decomposition of diacetone alcohol and in the hydrolysis of the carbethoxytrimethylammonium ion) the reactivity is entirely removed by association with metallic cations, indicating that these cations do not associate appreciably with the transition state. In the second (the alkaline hydrolysis of ethyl acetate) the association of the hydroxyl ion with the same metallic cations produced no decrease in reaction velocity, showing that the association persists in the transition state. The behaviour reported in the present paper is intermediate between these two extremes.

Apart from the overall discrepancy discussed above, the values of the dissociation constants of salts obtained from these kinetic measurements follow the same trend as those obtained by other methods. For each acid the zinc salts are much weaker than the calcium salts, and the calcium salts weaker than the barium salts, while for a given cation the dissociation constants follow the series : acetate > salicylate > mandelate; fumarate > malate.