5. The circumstances of the first determination of the isotopes of lead are given.

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[CONTRIBUTION FROM THE JOHNS HOPKINS UNIVERSITY, H. A. METZ LABORATORIES, INC., AND THE U. S. BUREAU OF STANDARDS]

III. THE REVERSIBLE ADDITION OF ETHYL ALCOHOL TO PARA-BROMOBENZONITRILE CATALYZED BY SODIUM, POTASSIUM AND LITHIUM ETHYLATES[1]

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RECEIVED JULY 26, 1928 PUBLISHED NOVEMBER 6, 1928

Introduction

In earlier papers of this series it was shown that the quantitative data available in sixty-two examples of different types of chemical changes can apparently be coördinated on the theory of the activity of both the ions and the non-ionized forms of electrolytes. This hypothesis was advanced in 1907 by Acree[2] and by Senter,[3] who did not have the good fortune to put it on a firm experimental basis supplied later by the co-workers[3] of Acree, Lapworth, Arrhenius, Goldschmidt, Bredig, Dawson and more recently Brönsted.

In the study of many of these reactions the solutions were fairly concentrated and varied from $N/1$ to $N/32$. Certain physical properties were therefore different from those in very low concentrations and were partly the cause of those deviations from the mass law which are called changes in activity, abnormal salt effects, etc. In the more concentrated solutions the ionic mobilities, viscosities and other physical factors can neither be considered the same as in the dilute solutions nor used without proper modifications in calculating the percentage of ionization of the ethylate or other electrolyte present.

In view of these facts it seemed desirable to investigate the catalytic activities of sodium, potassium and lithium ethylates in very dilute solu-

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[1] In memory of Ira Remsen.

[2] (a) Acree, *Am. Chem. J.*, **37**, 410 (1907); (b) **38**, 258 (1907); (c) **43**, 505 (1910); (d) **48**, 352, 368, 378 (1912); (e) **49**, 116, 127, 345, 369, 474 (1913); (f) THIS JOURNAL, **37**, 1902, 1909 (1915); (g) **38**, 2145 (1916); (h) **39**, 376 (1917); (i) *J. Phys. Chem.*, **19**, 381, 589 (1915); (j) **20**, 118, 353 (1916).

[3] (a) Senter, *J. Chem. Soc.*, **94**, 472 (1907); (b) Taylor and Arrhenius, *Mem. Nobelinst.*, **2**, Nos. 34, 35, 37; (c) Goldschmidt, *Z. Elektrochem.*, **15**, 6 (1909); (d) *Z. physik. Chem.*, **70**, 627 (1910); (e) Bredig, *Z. Elektrochem.*, **18**, 535, 543 (1912); (f) *Z. physik. Chem.*, **80**, 129, 170, 211 (1913); (g) Stieglitz, THIS JOURNAL, **34**, 1687, 1688, 1689, 1690, 1694 (1912); (h) **35**, 1774 (1913); (i) Dawson, *J. Chem. Soc.*, **103**, 2135 (1913); (j) **107**, 1426 (1915); (k) **130**, 2282 (1926); (l) Brönsted, THIS JOURNAL, **49**, 2554 (1927).

tions ($N/32$ to $N/2048$) having practically constant viscosities, ionic mobilities, etc., in order to see whether a simple relation exists between the reaction velocities and the conductivities of the ethylates and harmonizes with the idea of the possible activity of both the ethylate ions and the non-ionized ethylate molecules. The reaction chosen was the reversible addition of ethyl alcohol to *p*-bromobenzonitrile to form *p*-bromobenzimido ethyl ester in which the concentrations of the catalyzing sodium, potassium and lithium ethylates are not appreciably altered with time. Since this work was finished[4] a similar quantitative study by Gruse and Acree[5] has been interpreted on the basis that $N/32$ to $N/512$ solutions of sodium, potassium, and lithium ethylates may cause the inversion of *l*- to *d*-menthone.

Let us now examine the reaction velocities and conductivities of the different ethylates to see whether one possible interpretation of this reaction is that both the ethylate ions and the non-ionized ethylate molecules are catalytically active. Let α represent the ionized fraction, $(1 - \alpha)$ the un-ionized portion of the ethylate present in the concentration of one gram molecule in V liters. Let K_i' and K_i'' be the velocity constants for unit concentrations of ethylate ions in the two opposing reactions and K_m' and K_m'' be the corresponding constants for un-ionized ethylates. Let A be the original concentration (0.15 N in all cases) of the nitrile and X be that concentration of the imido ester formed in t minutes. Let $K_i = K_i' + K_i''$ and $K_m = K_m' + K_m''$. Let K_V be the velocity constant of the reaction when the ethylate is α ionized in N/V concentrations and call K_N the value of VK_V. Let $K = X/(A - X)$ at equilibrium or at infinite values of t. Then the correct differential equation for expressing the reaction is

$$\frac{dx}{dt} = [K_i'\alpha + K_m'(1 - \alpha)]\,(A - X(I/V) - [K_i''\alpha + K_m''(1 - \alpha)]\,[X/V] \quad (1)$$

On integration and collection of terms, this equation becomes

$$K_N/V = K_V = [K_i\,\alpha + K_m\,(1 - \alpha)]/V$$
$$= (1/t)\log\frac{KA}{KA - (K + 1)X} \quad (2)$$

in which the constants are really complex, as shown earlier.[6] But the use of Equation (2) should really give constant values[2b,e,5] for K_V and K_N for any given concentration of ethylate when proper data for t, K, A and X are inserted. From (2) we readily get

$$K_N = K_i\alpha + K_m\,(1 - \alpha) \quad (3)$$

for any ethylate. Our problem is to learn whether the value of K_i is

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[4] Acree, *Am. Chem. J.*, **49**, 127, 369 (1913).

[5] Gruse and Acree, This Journal, **39**, 376 (1917).

[6] Acree, *Am. Chem. J.*, **38**, 1 (1907); Birge and Acree, This Journal, **41**, 1031 (1919).

constant for the ethylate ions, coming alike from all ethylates, and whether the values for K_m for the three unlike ethylate molecules are positive and of about the same order of magnitude as K_i, and perhaps differ among themselves because of the influence of the different metals sodium, potassium and lithium within such molecules. But even though we are testing this theory, as have Brönsted and Dawson,[7,3e,i,j,k] again, recently, we have also suggested other mechanisms[2e,5] and have scrutinized[2b] various intermediate steps, the inter-relations of α, K_i, K_m and K_N,[8] and the possible activities of the cations and anions together.

Experimental Work

The *p*-bromobenzonitrile was prepared by treating cold diazotized pure *p*-bromoaniline slowly with a solution of solid cuprous cyanide dissolved in potassium cyanide. When distilled twice with steam, extracted in ether solution with dilute acid to remove any *p*-bromo-aniline and recrystallized from alcohol, a very white product is obtained with the melting point of 112.5° corrected. The ethyl alcohol was distilled twice from ignited calcium oxide as in earlier work[9,2i] and was 99.98% pure. Special experiments showed that the water need not be thoroughly removed as it does not here exhibit the marked influence shown in acid catalysis.

The concentration of the *p*-bromobenzonitrile was 0.15 N in all experiments. Sodium, potassium, lithium and thallium were dissolved in the pure cold alcohol and the ethylate solutions were made in duplicate and standardized as in the earlier work against hydrochloric acid accurately adjusted by gravimetric and volumetric methods. All volumetric glassware was accurately calibrated by the Bureau of Standards and by us. The very dilute ethylate solutions were made from the more concentrated ones by proper dilution with the pure alcohol while excluding the air. All ethylate solutions were rechecked just before use and were added to the nitrile solutions by means of a machine described earlier[10] for mixing solutions in proper amounts in flasks at the constant temperature of the reaction bath, 25°. When the desired reaction period had elapsed, the contents of the flasks were poured and washed into a slight excess of ice-cold standard hydrochloric acid in Erlenmeyer flasks and titrated back with standard alkali in the presence of methyl orange. By subtracting the known equivalent of the ethylate, the remaining acid used corresponded in cc. to the amount of imido ester, X, formed in t minutes or at equilibrium when $A = 30.00$ cc. expressed as possible complete transformation of the nitrile. The ester formed at equilibrium was about 27% of the maximum possible. The reaction velocity constants, K_V, were calculated by the special monomolecular formula in Equation (2), eliminating the equilibrium constants, and were then multiplied by V, the volume containing one gram mole of ethylate, to get K_N for a normal solution of ethylate having the α-ionization found for the $1/V$ concentration. Four tables, I, II, III and IV, are given here to show some of the representative data taken from the 75 tables marked out with sodium, potassium, lithium, thallium and tetramethylammonium ethylates. K_N and K_V are constant in all the tables. Data on the last two salts will be published when the conductivity and ionization measurements are completed. Tables V, VI, VII and VIII give the calculations of K_i and K_m and their relations to α and K_N for these three ethylates.

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[7] Brönsted and Dawson, *Z. physik. Chem.*, **108**, 185 (1924); **117**, 299 (1925).

[8] Ref. 2 e, p. 481, and above.

[9] Ref. 2 e, p. 493.

[10] Ref. 2 e, p. 490; 2 f, p. 1902.

Discussion and Interpretation of the Results

Tables V, VI, VII and VIII give a résumé of all the results obtained with sodium, potassium and lithium ethylates in concentrations varying from $N/32$ to $N/2048$. Similar results for much more concentrated solutions showing a salt effect will be given in another paper, together with data on added neutral salts. Each table gives the essential facts regarding V, α, $(1 - \alpha)$, the duplicate and average values for K_N calculated for all the different time periods used with each concentration of ethylate, the "K_N calculated" from $K_N = \alpha K_i + K_m (1 - \alpha)$ by substituting therein the values found for K_i and K_m for each ethylate in Table VIII, the experimental "Error in Per Cent," the percentage of the reaction αK_i due to the ethylate ions and the percentage of the reaction $(1 - \alpha) K_m$ due to the non-ionized ethylate molecules. Table VIII gives the individual and average values for the K_i and K_m calculated by solving all the pairs of simultaneous equations obtained by substituting the proper data for K_N and α in the equation $K_N = K_i \alpha + K_m (1 - \alpha)$. A study of all the tables will bring out a number of points bearing on the theory and discussed briefly in the summary.

TABLE I

0.15 N p-BROMOBENZONITRILE AND $N/64$ POTASSIUM ETHYLATE AT 25°. $A = 30.00$

T	x	K_V
29.5	1.21	0.00241
43.5	1.73	.00241
58.0	2.23	.00241
71.0	2.66	.00242
85.0	3.08	.00242
103.0	3.57	.00243
	Av. K_V	.00242
	$K_N =$	.1549

TABLE II

0.15 N p-BROMOBENZONITRILE AND $N/512$ POTASSIUM ETHYLATE AT 25°. $A = 30.00$

T	x	K_V
244	1.33	0.000309
289	1.55	.000308
325	1.73	.000308
372	1.93	.000307
428	2.20	.000309
489	2.45	.000309
	Av. K_V	.000308
	$K_N =$	.1577

TABLE III

0.15 N p-BROMOBENZONITRILE AND $N/32$ SODIUM ETHYLATE AT 25°. $A = 30.00$

T	x	K_V
15	1.08	0.00499
19	1.35	.00501
29	1.95	.00502
35	2.29	.00499
42	2.63	.00500
49.5	3.00	.00501
55	3.23	.00500
	Av. K_V	.00500
	$K_N =$	.1600

TABLE IV

0.15 N p-BROMOBENZONITRILE AND $N/2048$ LITHIUM ETHYLATE AT 25°. $A = 30.00$

T	x	K_V
1303	1.12	0.000076
1363	1.16	.000076
1500	1.29	.000077
1571	1.35	.000078
1707	1.45	.000078
2807	2.14	.000076
4320	2.89	.000076
	Av. K_V	.000077
	$K_N =$	.1577

TABLE V

EXPERIMENTAL VALUES OF K_N FOR SODIUM ETHYLATE AND *p*-BROMOBENZONITRILE AND FOR THE IONIZATION OF SODIUM ETHYLATE IN ABSOLUTE ALCOHOL AT 25°

V	α	$1 - \alpha$	K_N	K_N, av.	K_N, calcd.	Error, %	Reaction due to αK_i, %	Reaction due to $(1 - \alpha)$ K_m, %
32	0.5771	0.4229	0.1600, 0.1600	0.1600	0.1596	+0.20	58.07	41.91
64	.6777	.3223	0.1598, 0.1594, .1604, 0.1600	.1599	.1598	.00	68.10	31.90
128	.7723	.2277	.1600, 0.1600	.1600	.1601	.00	77.47	22.53
256	.8714	.1286	.1643, 0.1620	.1632	.1603	+1.81	87.30	12.70
512	.9449	.0551	.1602, 0.1597, .1603	.1600	.1604	−0.25	94.61	5.39
1024	.9819	.0181	.1604, 0.1608, .1603	.1605	.1605	.00	98.25	1.75
2048	.9819	.0021	.1577, 0.1556	.1567	.1606	−2.43	99.79	0.21

TABLE VI

EXPERIMENTAL VALUES OF K_N FOR POTASSIUM ETHYLATE AND *p*-BROMOBENZONITRILE AND FOR THE IONIZATION OF POTASSIUM ETHYLATE IN ABSOLUTE ALCOHOL AT 25°

V	α	$1 - \alpha$	K_N	K_N, av.	K_N, calcd.	Error, %	Reaction due to αK_i, %	Reaction due to $(1 - \alpha)$ K_m, %
32	0.5790	0.4210	0.1449, 0.1449, .1456	0.1451	0.1548	−6.27	60.93	39.07
64	.6739	.3261	.1549, 0.1555, .1542, 0.1555	.1550	.1566	−0.89	70.10	29.90
128	.7675	.2325	.1626, 0.1651	.1629	.1584	+3.03	78.93	21.07
256	.8546	.1454	.1687, 0.1697, .1702	.1695	.1601	+5.87	88.95	11.05
512	.9234	.0766	.1587, 0.1577	.1582	.1614	−1.98	93.19	6.81
1024	.9745	.0255	.1556, 0.1587	.1571	.1624	−3.28	97.75	2.25
2048	.9993	.0007	.1556	.1536	.1629	−4.48	99.93	0.07

TABLE VII

EXPERIMENTAL VALUES OF K_N FOR LITHIUM ETHYLATE AND *p*-BROMOBENZONITRILE AND FOR THE IONIZATION OF LITHIUM ETHYLATE IN ABSOLUTE ALCOHOL AT 25°

V	α	$1 - \alpha$	K_N	K_N, av.	K_N, calcd.	Error, %	Reaction due to αK_i, %	Reaction due to $(1 - \alpha)$ K_m, %
32	0.4553	0.5447	0.1187, 0.1184	0.1188	0.1232	−3.72	58.71	41.29
64	.5624	.4376	.1293, 0.1286	.1290	.1303	−1.00	68.58	31.42
128	.6775	.3225	.1382, 0.1357	.1370	.1390	−1.44	77.45	22.55
256	.7865	.2135	.1439, 0.1439	.1439	.1449	−0.65	86.21	13.79
512	.8855	.1145	.1562, 0.1567	.1564	.1514	+3.30	92.94	7.06
1024	.9579	.0421	.1505, 0.1516	.1511	.1561	−3.30	97.51	2.49
2048	1.0000	.0000	.1577	.1577	.1589	−0.76	100.00	0.00

TABLE VIII

EXPERIMENTAL VALUES OF K_i AND K_m FOUND FOR SODIUM ETHYLATE, POTASSIUM ETHYLATE AND LITHIUM ETHYLATE AND 0.15 N p-BROMOBENZONITRILE AT 25°

	Sodium ethylate		Potassium ethylate		Lithium ethylate	
V	K_i	K_m	K_i	K_m	K_i	K_m
V = 32 : V = 64	0.1596	0.1606	0.1889*	0.08347*	0.1715*	0.07439*
V = 32 : V = 128	.1600	.1600	.1848	.09042	.1637	.08090
V = 32 : V = 256	.1646	.1537	.1823	.09383	.1602	.08382
V = 32 : V = 512	.1600	.1600	.1611	.12300	.1665	.07859
V = 32 : V = 1024	.1603	.1593	.1578	.12750	.1538	.08916
V = 32 : V = 2048	.1567	.1645	.1556	.13060	.1577	.08592
V = 64 : V = 128	.1602	.1592	.1825*	.09595*	.1594*	.08991*
V = 64 : V = 256	.1654	.1484	.1810	.10180	.1581	.09161
V = 64 : V = 512	.1600	.1596	.1591	.14700	.1661	.08131
V = 64 : V = 1024	.1605	.1586	.1572	.15090*	.1535	.09757
V = 64 : V = 2048	.1567	.1667	.1556	.15430	.1577	.09212
V = 128 : V = 256	.1674	.1851	.1805*	.10590*	.1574*	.09411*
V = 128 : V = 512	.1600	.1600	.1555	.18604	.1671	.07381
V = 128 : V = 1024	.1605	.1582	.1564	.18445	.1532	.10293
V = 128 : V = 2048	.1567	.1713	.1556	.18664	.1577	.09351
V = 256 : V = 512	.1576*	.2011*	.1456*	.30980*	.1709*	.04459*
V = 256 : V = 1024	.1601*	.1845*	.1544*	.25780*	.1529	.11086
V = 256 : V = 2048	.1566*	.2080*	.1555*	.25150*	.1577	.09306
V = 512 : V = 1024	.1607*	.1472*	.1565*	.17600*	.1480*	.22122*
V = 512 : V = 2048	.1566*	.2188*	.1555	.18980*	.1577	.14634
V = 1024 : V = 2048	.1562*	.3937*	.1555*	.21800*	.1577*	.00093
Average[a]	.1598	.1799	.1637	.16022	.15945	.09179
	(.159)	(.174)				
Average unmarked values	.1605	(.1616)	.1629	.14356	.15891	.09343
		.163				

[a] The averages given in the parentheses include some of the data left out of these tables because of lack of space.

Summary

1. The velocity of the reversible addition of ethyl alcohol to p-bromobenzonitrile at 25° has been measured in solutions of sodium, potassium and lithium ethylates in concentrations varying from $N/32$ to $N/2048$ to learn whether both the ethylate ion and the cations and the non-ionized ethylate molecules are catalytically active.

2. By substituting all the different values of α and K_N in the equation $K_N = K_i \alpha + K_m (1 - \alpha)$, we obtain a series of simultaneous equations whose solution gives us the corresponding individual and best average values for K_i and K_m for each ethylate in Table VIII.

3. It is found that the constants expressing the activity of the ethylate ion in unit concentration are the same for all three ethylates within the inherent experimental errors of about 2%. These values for K_i are about 0.161, 0.163 and 0.159 for sodium, potassium and lithium ethylates, respectively. The corresponding values for K_m are 0.163, 0.144 and 0.093.

This value of K_i is the sum of the activities of the ethylate ion in the two opposing reactions and K_m is the corresponding sum of the activities of the non-ionized metallic ethylate; both constants are independent of the equilibrium constant.

4. The substitution of these values of K_i and K_m for each ethylate in the above Equation (3) gives calculated values for K_N, which agree on the average with the experimental data within about 2% for all concentrations from $N/32$ to $N/2048$ (see Tables V, VI and VII).

5. By the use of this theory of catalysis and these values for K_i and K_m for the different ethylates, we can explain in a satisfactory manner the fact that the values of K_N are practically independent of α and dilution of sodium ethylate from $N/32$ to $N/2048$; change only slightly for potassium ethylate; increase 34% for lithium ethylate; and become substantially identical for all three of these alcoholate bases at $N/2048$ when only ethylate ions are present (see Tables V, VI and VII).

6. The above facts and studies with added halogen salts of these metals in dilute and concentrated solutions of ethylates show that in these dilute solutions any possible activity of the metal cations may be disregarded. In the more concentrated solutions a salt effect becomes apparent.

7. The broad equations have been developed for applying this theory of ion mole activity to reversible monomolecular reactions and determining the relation of the equilibrium and total velocity constants to the ionization of the catalyst and its separate ionic and molecular activities for the two opposing reactions. The same idea can be applied to all other reactions in pure or pseudo catalysis.

8. These conclusions agree with the application of this ion mole theory of catalysis to sixty-two quantitative studies of (*a*) reactions worked out by our associates and (*b*) our re-interpretations of the work of other investigators.

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