measurements of the reduction of sulfur dioxide by carbon monoxide. The details of the calculation and the tabulated results are presented.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

STUDIES IN CONDUCTIVITY. IV. THE CONDUCTIVITY OF ALKALINE EARTH FORMATES IN ANHYDROUS FORMIC ACID.

BY H. I. SCHLESINGER AND R. D. MULLINIX.[1]

Received November 15, 1918.

In previous work[2] on the behavior of the alkali metal formates dissolved in (anhydrous) formic acid, it was shown that when the degree of ionization is calculated from the conductivity uncorrected for viscosity, these very highly dissociated salts obey the law of chemical equilibrium up to relatively high concentrations. It was therefore considered important to investigate also some of the formates of bivalent metals, especially as there lay in this direction a possibility that light might be shed on the problem of the existence of intermediate ions in highly ionized salts. For this purpose we chose the formates of the alkaline earth metals.

The method and apparatus for preparing the formic acid and for making the conductivity measurements are described in a paper of this series by Schlesinger and Reed.[3] Calcium formate was prepared from a Kahlbaum sample by recrystallization until no further change in the conductivity resulted. The stronium salt was prepared by dissolving the carbonate in an aqueous solution of formic acid and evaporating the resulting solution, recrystallizing the resulting salt and drying it at a sufficiently high temperature to drive out the water. While all of the salts were analyzed and found pure within the limits of the ordinary analytical error, we used as criterion of their purity the fact that further recrystallizations produced no change in the conductivity of the salts when made up to a definite concentration in formic acid solutions.

In Tables I and II are given the experimental results found for calcium and strontium formate solutions, respectively. In the first column of each table is given the concentration c expressed in gram equivalents per liter, in the second column the specific conductivity χ in reciprocal ohms, in the third column the specific conductivity in reciprocal ohms

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[1] The work herein reported forms a part of a thesis presented by R. D. Mullinix to the faculties of the Ogden Graduate School of Science of the University of Chicago in part fulfilment of the requirements for the Degree of Doctor of Philosophy. The experimental work was completed in the spring of 1917.

[2] THIS JOURNAL, 36, 1599 (1914); 38, 271 (1916).

[3] To be published in THIS JOURNAL in the near future.

corrected for the conductivity of the acid used as a solvent,[1] in the fourth

TABLE I.

Conductivity of Solutions of Calcium Formate in Anhydrous Formic Acid at 25°.

C.	κ.	κ_a.	$100\lambda_a$.	λ_a.	α.	k.
0.0000	.....	.....	1.8190	54.98	..	...
0.0415	0.0022252	0.0021622	1.9195	52.10	..	...
0.0646	0.0032420	0.0031808	2.0313	49.23	..	...
0.0784	0.0038153	0.0037541	2.0874	47.91	..	...
0.0951	0.0044780	0.0044150	2.1547	46.41	0.844	(0.435)
0.0969	0.0045564	0.0044830	2.1621	46.25	0.8413	(0.432)
0.1175	0.0053324	0.0052693	2.2310	44.82	0.8153	0.423
0.1461	0.0063716	0.0063085	2.3154	43.19	0.7856	0.421
0.1545	0.0066671	0.0066041	2.3395	42.74	0.7775	0.420
0.1650	0.0070468	0.0069834	2.3648	42.29	0.7692	0.423
0.1874	0.0077918	0.0077288	2.4248	41.24	0.7502	0.422
0.2043	0.0083288	0.0082655	2.4685	40.51	0.7369	0.422
0.2166	0.0087250	0.0086638	2.4994	40.01	0.7277	0.421
0.2498	0.009752	0.009687	2.5787	38.78	0.7054	0.422
0.2808	0.0106605	0.0105993	2.6491	37.75	0.6866	0.422
0.2979	0.0111495	0.0110885	2.6865	37.22	0.6771	0.423
0.3111	0.011508	0.011447	2.7176	36.80	0.6693	0.422
0.3202	0.011762	0.011700	2.7367	36.54	0.6647	0.422
0.3533	0.012641	0.012579	2.8087	35.60	0.6476	0.421
0.3778	0.013260	0.013197	2.8625	34.93	0.6355	(0.419)
0.3899	0.013563	0.013500	2.8878	34.63	0.6299	(0.418)
0.4362	0.014690	0.014627	2.9823	33.53	0.6099	(0.416)
0.4527	0.015065	0.015002	3.0178	33.14	0.6028	(0.414)
0.4925	0.015932	0.015869	3.1037	32.20	0.5861	(0.409)

TABLE II.

Conductivity of Solution of Strontium Formate in Anhydrous Formic Acid at 25°.

C.	κ.	κ_a.	$100/\lambda_a$.	λ_a.	α.	k.
0.0000	....	....	1.7582	56.876	..	...
0.0360	0.002039	0.001978	1.8206	54.928	0.9657	(0.979)
0.0476	0.002610	0.002549	1.8666	53.574	0.9419	(0.727)
0.0672	0.003525	0.003467	1.9404	51.536	0.9061	(0.587)
0.0964	0.004785	0.004724	2.0415	48.983	0.8612	(0.515)
0.1117	0.005426	0.005365	2.0825	48.020	0.8443	(0.511)
0.1380	0.006475	0.006413	2.1512	46.486	0.8173	0.505
0.1604	0.007343	0.007282	2.2032	45.389	0.7980	0.506
0.1784	0.008016	0.007956	2.2430	44.583	0.7839	0.507
0.1868	0.008312	0.008251	2.2634	44.181	0.7768	0.505
0.2358	0.010019	0.009959	2.3673	42.243	0.7427	0.505
0.2565	0.010725	0.010664	2.4054	41.573	0.7309	0.509
0.2718	0.011207	0.011146	2.4390	41.001	0.7209	0.506
0.3001	0.012106	0.012045	2.4911	40.143	0.7058	0.508
0.3149	0.012549	0.012488	2.5213	39.663	0.6973	0.506
0.3443	0.013418	0.013357	2.5777	38.796	0.6821	(0.504)
0.3859	0.014578	0.014517	2.6579	37.637	0.6617	(0.499)

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[1] The specific conductivity of the acid used for these experiments averaged about 6.3×10^{-5}.

column the corrected equivalent conductivity λ_a, in the fifth column 100 divided by the equivalent conductivity, in the sixth column a, which is a calculated value which corresponds to what would be the degree of ionization for the case of the uni-univalent salts and which we obtained in the manner described below, and in the sixth column K, a constant over a certain range of the concentrations investigated, calculated as explained later.

For the purpose of interpreting our experimental data, we followed the method used in the earlier papers. It is possible to cast the mass law for uni-bivalent salts into a form in which suitable plotting would result in a straight line if the mass law were obeyed. Our data plotted in this way did not give a straight line. It occurred to us that the cause of this lack of agreement might be ionization into an intermediate ion—in the case of the calcium formate, for example into $CaOCHO^+$ and $OCHO^-$. We therefore plotted the values of $100/\lambda$ against λ, which according to the equation $1/\lambda = 1/\lambda_0 + (1/K\lambda_0^2)c\lambda$ gives a straight line in the cases of uni-univalent salts which obey the mass law. These plots are shown in Fig. 1. For the purpose of comparison, the corresponding curve for sodium formate, taken from the work of Schlesinger and Reed,[1] has been added.

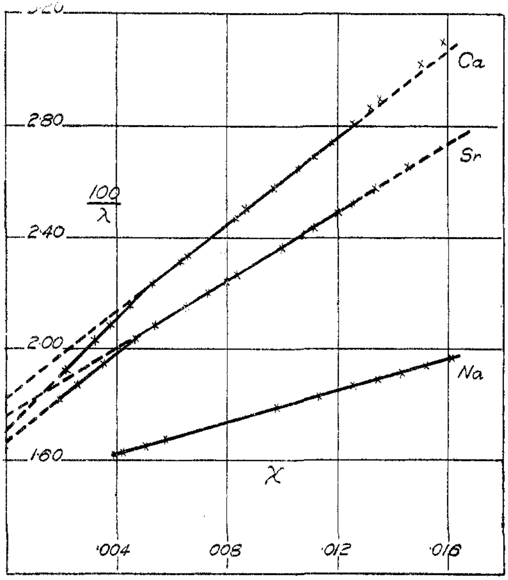

Fig. 1.

It will be seen that the curves for the alkaline earth formates differ in some respects from those obtained for the uni-univalent salts. The latter are straight lines, without a break from the lowest concentrations which have thus far been accessible to reliable measurement to a concentration varying from 0.28 to above 0.45 normal in the different salts. At higher concentrations a deviation of a nature to be expected[2] has been observed for all of the uni-univalent salts investigated. The curves for the alkaline earth formates on the other hand consist of three sections. The portion of the curve representing the lower concentrations consists, so far as the

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[1] *Loc. cit.*

[2] Schlesinger and Martin, THIS JOURNAL, **36**, 1599 (1914).

data now available indicate, of two straight lines which intersect at a concentration in the neighborhood of 0.1 equivalent. From this point of intersection upward the curves for these salts are in all respects like those for the alkali metal formates.[1] It is therefore clear that two sets of values can be found for the terms λ_0 and K in the equation given on a previous page. The values calculated for the tables are those referring to the points on the middle portion of each of the curves.

We are as yet unable to give a satisfactory explanation of the behavior of these alkaline earth formates. It is quite likely that these salts ionize into a metal formate ion which in the more dilute solutions is somewhat decomposed into the simple metal ion and that this second ionization becomes sufficiently great at the concentration where the two lines intersect to effect the conductivity appreciably. It is not clear why, if this interpretation is correct, there should be a sharp break at this point. It was our intention to investigate these questions further by studies on the solubilities of these formates in the presence of salts with common ions and also to make possible the measurement of the conductivities at still lower concentrations by reducing the conductivity of the solvent by new means which have been partially worked out, but this intention was frustrated by the necessity of taking up work of more immediate importance in connection with the war. While this work is therefore in a sense incomplete it was thought desirable to publish it in its present form because reference has to be made in the data here presented in the next two papers of this series which are to be published soon.

CHICAGO, ILLINOIS.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE ARKANSAS AGRICULTURAL EXPERIMENT STATION AND OF THE JOHNS HOPKINS UNIVERSITY.]

THE IDENTIFICATION OF ACIDS. IV. PHENACYL ESTERS.

BY J. B. RATHER[2] AND E. EMMET REID.

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In several recent papers[3] *p*-nitrobenzyl esters of a large number of acids have been described, and it has been shown that such esters are readily formed and that many of them are useful for identification purposes; but some of the esters melted too low, some too high, and others had undesirable properties. The presence of the nitro group leads to

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[1] In the reproduction of the curve for sodium formate, the upper portion which deviates from the straight line is not shown.

[2] The experimental work described in this paper, except that relating to the preparation of the reagent and that with phenacyl chloride was carried out in the laboratory of the Department of Agricultural Chemistry of the Arkansas Agr. Exp. Station. Thanks are due to Prof. J. Sam Guy of the University of Arkansas for some of the acids used.

[3] THIS JOURNAL, **39**, 124, 304, 701, 1727 (1917).