points on the two lower curves for which $\lambda_{Cl} > 62$ can be thus transposed, computations with the available data indicate that the curves may be thus superposed to higher concentrations.

Summary

Measurements of the transference numbers at 25° of aqueous solutions of lanthanum chloride by the method of moving boundaries have been made. The chloride ion conductances of these solutions have been compared with similar measurements of solutions of calcium chloride and sodium chloride. From this comparison an empirical rule for the effect of the valence of the co-ion on the chloride ion conductance has been obtained.

NEW YORK, N. Y. RECEIVED OCTOBER 15, 1938

[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

The Electrolytic Conductivity of Zinc Sulfate and Copper Sulfate in Water at 25°[1]

BY BENTON BROOKS OWEN AND ROBERT W. GURRY[2]

Within the last decade the conductivities of a large number of electrolytes have been precisely redetermined at 25°. Most of these modern measurements have been confined to 1–1 and 2–1 valence types because they conform to the requirements of the inter-ionic attraction theory at experimentally accessible dilutions, and may therefore be readily extrapolated. The 3–1 electrolyte lanthanum chloride can possibly be satisfactorily extrapolated along the Onsager[3] slope, but no 2–2 electrolyte has yet been found amenable to this simple treatment. The extrapolation of the conductivities of zinc and copper sulfates is of particular interest because of the complications introduced by relatively large departures from the limiting slope and partial hydrolysis of the ions.

In the present research we have carefully measured the specific conductivity and *p*H of dilute solutions of these salts at 25°, and made what we believe to be adequate solvent and hydrolysis corrections. The results have been extrapolated by a number of methods fulfilling the requirements of the inter-ionic attraction theory, and which lead to essentially the same values of Λ_0. Zinc and copper sulfates are particularly well suited for this type of investigation because they can be highly purified, and their hydrolysis corrections are not too great to be estimated with sufficient accuracy. Furthermore, the supplementary thermodynamic and conductance data required in our calculations are available for these salts, and for the sulfate and hydrosulfate ions.

Materials and Technique

Merck reagent grade zinc sulfate heptahydrate was recrystallized twice from a mixture of highly purified methanol and water, and then twice from conductivity water. The last crystallization was accomplished by partial evaporation of the water at room temperatures with the necessary precautions against contamination by dust.

Merck reagent grade copper sulfate pentahydrate was recrystallized four times from conductivity water. The purified salt was crushed in an agate mortar and dried over a mixture of the penta- and trihydrates.

Stock solutions, 0.1 and 0.5 *m*, were prepared by weight and checked by gravimetric analysis. Vacuum corrections were applied throughout. Samples of the zinc sulfate solutions were evaporated at 95° and the salt dehydrated at 300° and weighed as $ZnSO_4$. The copper was determined electrolytically, with the last traces precipitated as sulfide and weighed as oxide. All duplicate analyses checked within 0.02% from the means.

The Dike[4] bridge was operated by a vacuum tube oscillator at 1000 cycles. It was calibrated against Bureau of Standard resistors with a d. c. source and a sensitive galvanometer. All measurements reported were made without shunts, and were reproducible to 0.002%.

The temperature was adjusted to 25 ± 0.005° with a platinum resistance thermometer certified by the Bureau of Standards, and thermoregulation within 0.005° was maintained during the course of the measurements.

The cells were the type B[5] generally employed in this Laboratory. The electrodes were lightly platinized. Cell constants were determined several times during the course of the measurements with 0.1 demal potassium chloride according to Jones and Bradshaw.[6] The cell constants, l/a, were 4.5221 for cell III and 3.7260 for cell IV. The specific conductivity of the water employed was usually less than 2×10^{-7} mho.

The *p*H values required for the solvent and hydrolysis corrections were obtained colorimetrically by the use of LaMotte indicator standards in the zinc sulfate solutions, and electrometrically with glass electrodes[7] in the copper

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[1] This communication embodies part of the experimental material contained in the thesis submitted by Robert W. Gurry to the Graduate School of Yale University in partial fulfilment of the requirements for the degree of Doctor of Philosophy (1937).

[2] Present address: Research Laboratory, United States Steel Corp., Kearny, N. J.

[3] Onsager, *Physik. Z.*, **27**, 388 (1926).

[4] Dike, *Rev. Sci. Instruments*, **2**, 379 (1931).

[5] Saxton and Meier, THIS JOURNAL, **56**, 1918 (1934).

[6] Jones and Bradshaw, *ibid.*, **55**, 1780 (1933).

[7] The authors are indebted to Professor Leslie F. Nims of the Department of Physiology for making these measurements.

sulfate solutions. The results were plotted on a large scale against $\sqrt{C}$ for interpolation at the required concentions. The pH at even values of $\sqrt{C}$ are recorded in Table III. The acidity of dilute zinc sulfate solutions has been studied recently by Kolthoff and Kameda[8] by both colorimetric and electrometric methods. Their pH values are about 0.1 unit lower than ours, but in view of the sensitivity of these unbuffered solutions to acid and basic impurities, this concordance seems satisfactory.

Experimental Results

The experimental data are recorded in Tables I and II as specific conductivities, κ, at the concentrations, C, in moles per liter of solution. The specific conductivity of the solvent, κ_0, and the cell constant, l/a, employed in each run are given at the bottom of the columns of data to which they apply.

TABLE I

SPECIFIC CONDUCTIVITY OF $ZnSO_4$ SOLUTIONS AT 25°

	10^3C	$10^3\kappa$	10^3C	$10^3\kappa$	10^3C	$10^3\kappa$
	0.3880	0.09163	0.4168	0.09794	0.5474	0.12578
	.8532	.18766	.8614	.18933	2.2411	.43547
	1.5397	.31549	1.5063	.30959	4.6463	.79904
	2.3748	.45728	2.3717	.45684	8.4433	1.29735
	3.6786	.65980	3.6724	.65892	16.001	2.15505
	5.3712	.90040	5.0718	.85930	24.043	2.96765
	6.9412	1.10832	6.8254	1.09342	32.590	3.7658
	9.6428	1.44269	8.6867	1.32720	41.965	4.5894
	14.3990	1.98308	11.0427	1.60707	50.634	5.3156
	18.7372	2.44029	15.6522	2.11795	60.826	6.1356
			19.8362	2.55188	73.563	7.1195
					85.773	8.0279
					108.509	9.6463
					128.845	11.0273
$10^7\kappa_0$	0.955		1.534		1.471	
l/a	4.5221		3.7260		3.7260	

TABLE II

SPECIFIC CONDUCTIVITY OF $CuSO_4$ SOLUTIONS AT 25°

	10^3C	$10^3\kappa$	10^3C	$10^3\kappa$	10^3C	$10^3\kappa$
	0.3958	0.09375	0.3970	0.09403	0.4945	0.11496
	.9365	.20341	.8572	.18813	2.0470	.39918
	1.8740	.37032	1.3995	.28858	5.0349	.83767
	2.6890	.50136	1.9966	.39071	8.8474	1.31259
	3.6512	.64521	3.0281	.55323	13.002	1.77552
	4.7890	.80429	4.1282	.71314	17.808	2.26833
	6.4517	1.02163	5.5098	.90042	24.175	2.87538
	8.1945	1.23519	7.1003	1.10255	31.650	3.5428
	10.1478	1.46193	9.5816	1.39739	39.870	4.2369
	12.6639	1.73870	11.7779	1.64307	47.151	4.8258
	15.0319	1.98787			55.680	5.4912
					66.573	6.3100
					77.414	7.0973
					97.393	8.4905
					115.265	9.6845
$10^7\kappa_0$	1.861		2.073		2.780	
l/a	4.5221		3.7260		3.7260	

Although the specific conductivities are known to within 0.01%, the calculated equivalent conductivities are less accurate because of the uncertainties in the solvent and hydrolysis corrections. The maximum values of these combined corrections are about 0.2 and 0.8 conductance units in the zinc and copper solutions, respectively.

The solvent conductance was assumed to be due to hydrogen and hydroxyl ions from the ionization of the water, and a constant residual specific conductance, δ, due to unknown impurities. The latter was estimated by subtracting the specific conductance of pure water, 0.546×10^{-7}, from the measured solvent conductance, κ_0. Then. as the pH of the water was altered by hydrolysis of the salt being studied, the correction for solvent conductance becomes

$$1000\,\Delta\kappa_1 = \lambda_H C_H + \lambda_{OH} C_{OH} + 1000\delta \tag{1}$$

For this correction we used $\lambda_H = 350$ and $\lambda_{OH} = 200$. The concentrations, C_H and C_{OH}, were determined from the pH values given in Table III. The equivalent conductance corrected for solvent is then given by

$$\Lambda_1 = \frac{1000\kappa}{2C} - \frac{1000\,\Delta\kappa_1}{2C} \tag{2}$$

The variation of pH with total salt concentration is due to hydrolysis of the bivalent ions, and can be expressed as follows

$$Zn^{++} + H_2O \rightleftarrows Zn(OH)^+ + H^+$$

and

$$SO_4^= + H_2O \rightleftarrows HSO_4^- + OH^-$$

The formation of H_2SO_4 and $Zn(OH)_2$, or more complex ions, was assumed to be negligible in dilute solutions.

Since we are concerned with obtaining the conductance due to Zn^{++} and $SO_4^=$ ions only, it is necessary to correct the apparent equivalent conductivity, Λ_1, for the decrease due to replacement of a small fraction of the bivalent ions by the monovalent complex ions $Zn(OH)^+$ and HSO_4^-. The correction to be added is

$$1000\,\Delta\kappa_2 = C_{ZnOH^+}(2\lambda_{Zn^{++}} - \lambda_{ZnOH^+}) + C_{HSO_4^-}(2\lambda_{SO_4^=} - \lambda_{HSO_4^-}) \tag{3}$$

Accordingly the desired equivalent conductance of (unhydrolyzed) zinc sulfate is given by

$$\Lambda = \Lambda_1 + \frac{1000\,\Delta\kappa_2}{2C} \tag{4}$$

The equivalent conductances of the ions were taken as 79.8 and 50 for $SO_4^=$ and HSO_4^-; 53.5 and 32.1 for Zn^{++} and $ZnOH^+$; and 52.0 and 31.2 for Cu^{++} and $CuOH^+$. According to our final results $\lambda_{Cu^{++}}$ should have been nearer 54, but it would be useless to revise the corrections on this basis because λ for $ZnOH^+$ and $CuOH^+$ were merely assumed to be 0.6 of the values of the corresponding divalent ions by analogy with the

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(8) Kolthoff and Kameda, THIS JOURNAL, **53**, 832 (1931).

findings of Chandler[9] and Jeffery and Vogel[10] in dealing with organic acids.

The complex univalent ion concentrations were estimated as follows. The HSO_4^- concentration was calculated from the measured *p*H and the stoichiometric $SO_4^=$ concentration, using 0.012 as the ionization constant[11] of the hydrosulfate ion, and disregarding activity coefficients. The $ZnOH^+$ (or $CuOH^+$) concentration was then found by adding the difference $C_{H^+} - C_{OH^-}$ to the HSO_4^- ion concentration, since the $ZnOH^+$ (or $CuOH^+$) and HSO_4^- concentrations would be equal at exact neutrality.

The final equivalent conductances corrected by equation (4) were interpolated graphically at even values of $\sqrt{C}$, and recorded in Table III. For this purpose we used a very large scale plot of Λ *vs.* $\sqrt{C}$ with a stiff spline, and also several plots of deviation functions of the type $[\Lambda + A\sqrt{C} - BC]$ *vs.* $\sqrt{C}$ to expose errors in curve fitting. The discordance between the values read from two curves was never greater than 0.02 conductance unit, and since this is probably the order of the uncertainty in the combined corrections used in calculating Λ, these smoothed values will be used in the extrapolations to follow.

TABLE III

INTERPOLATED VALUES OF THE *p*H AND EQUIVALENT CONDUCTIVITY

	$ZnSO_4$		$CuSO_4$	
$\sqrt{C}$	*p*H	Λ	*p*H	Λ
0.02	6.41	117.61	5.73	117.52
.025	6.37	113.33	5.57	112.89
.03	6.34	109.25	5.46	108.55
.04	6.29	101.86	5.32	100.74
.05	6.25	95.49	5.22	94.07
.06	6.21	89.99	5.15	88.35
.07	6.17	85.20	5.09	83.43
.08	6.14	81.08	5.05	79.17
.10	6.09	74.24	4.99	72.20
.12	6.04	68.86	4.95	66.72
.14	6.00	64.49	4.92	62.33
.16	5.96	60.89	4.89	58.74
.18	5.93	57.85	4.87	55.72
.20	5.90	55.26	4.84	53.16
.22	5.86	53.02	4.81	50.95
.24	5.83	51.04	4.78	49.03
.26	5.80	49.31	4.76	47.33
.28	5.78	47.71	4.74	45.83
.30	5.76	46.27	4.71	44.48
.32	5.73	45.02	4.69	43.25
.34	5.71	43.83	4.66	42.13

Extrapolations and Discussion

In the extrapolation of activity coefficient data for bi-bivalent electrolytes the initial departures from the limiting slope may be taken into account by the inclusion of higher terms[12,13] in the Debye–Hückel equation, or by the introduction of a dissociation constant to allow for the effect of relatively stable ion-pairs upon the ionic distribution.[14,15] In the absence of a numerical development of the higher terms for the Onsager equation, the modern extrapolation of bi-bivalent conductance data has always involved the concept of incomplete dissociation.

There are two techniques available for evaluating the dissociation constant, K. Onsager[16] and Davies[17] estimate K at each concentration. Fuoss and Kraus[18] determine it graphically from the slope of a suitable extrapolation function. This procedure has been greatly simplified by Fuoss,[19] and recently extended to higher concentrations by Shedlovsky.[20] All of these methods are based upon some assumption regarding the conductance, Λ_i, of the hypothetical completely ionized electrolyte. It may be assumed to obey the limiting law at the lowest experimental concentrations, or approach it asymptotically according to some arbitrary empirical function. In the extrapolation of our data we have used the limiting law and most of the empirical extensions employed for this purpose. Although all extrapolations give values of Λ_0 agreeing within 0.6 conductance unit, the apparent variation in K is over 20%, being very sensitive to the manner in which Λ_i is assumed to approach the limiting law.

In Fig. 1 we have illustrated the extrapolations which we consider most satisfactory. The open circles represent the smoothed results of Table III plotted to conform to the Fuoss[19] function

$$\Lambda/F_{(z)} = \Lambda_0 - (C\vartheta^2 y^2_{\pm})\Lambda_0/K \qquad (5)$$

and the dots are calculated according to the modification

$$\Lambda S_{(z)} = \Lambda_0 - (C\vartheta^2 y^2_{\pm})\Lambda_0/K \qquad (6)$$

proposed by Shedlovsky.[20] Equation (5) assumes the limiting law, and equation (6) allows for

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[9] Chandler, THIS JOURNAL, **30**, 694 (1908).

[10] Jeffery and Vogel, *J. Chem. Soc.*, **137**, 21 (1935).

[11] Hamer, THIS JOURNAL, **56**, 860 (1934).

[12] Gronwall, La Mer and Sandved, *Physik. Z.*, **29**, 358 (1928).

[13] Müller, *ibid.*, **28**, 324 (1927).

[14] Bjerrum, *Kgl. Danske Videnskb. Selskab, Math.-fys. Medd.*, **7**, No. 9 (1926).

[15] Fuoss and Kraus, THIS JOURNAL, **55**, 1019 (1933).

[16] Onsager, *Physik. Z.*, **27**, 277 (1927).

[17] Davies, *Trans. Faraday Soc.*, **23**, 351 (1927).

[18] Fuoss and Kraus, THIS JOURNAL, **55**, 476 (1933).

[19] Fuoss, *ibid.*, **57**, 448 (1935).

[20] Shedlovsky, *J. Franklin Inst.*, **225**, 739 (1938).

slight positive deviations from the limiting law by multiplying the slope by the factor Λ/Λ_0 which rapidly approaches unity at high dilutions. In both of these equations $Z = (\alpha\Lambda_0 + \beta)\,\Lambda_0^{-3/2}\sqrt{C}$, ϑ is the degree of dissociation, and $y_{\pm}$ is the mean ionic activity coefficient. The function

$$F_{(z)} = 1 - Z(1 - Z(1 - Z(1 - \ldots)^{-1/2})^{-1/2})^{-1/2} \tag{7}$$

is tabulated by Fuoss,[19] and the corresponding function of Shedlovsky[20] is given by

$$S_{(z)} = 1 + Z + \frac{Z^2}{2} + \frac{Z^3}{8} - \ldots \tag{8}$$

In the calculation of Z, we have used $\Lambda_0 = 132.8$ for zinc sulfate, $\Lambda_0 = 133.6$ for copper sulfate, and the theoretical values $\alpha = 1.8215$ and $\beta = 239.40$. It was not necessary to calculate the value of ϑ ($\vartheta = \Lambda/\Lambda_0\ F_{(z)} = \Lambda S_{(z)}/\Lambda_0$) because accurate values of the stoichiometrical activity coefficient, $y_{\text{stoi.}} = \vartheta y_{\pm}$, are available[21-23] for zinc sulfate, and the values for copper sulfate are known[24] to be very similar. In the calculation of $y_{\text{stoi.}}$ at the concentrations required for our purposes, we used the extended terms[12] and an "a" value of 3.64 Å.[22]

Inspection of Fig. 1. shows that the plots according to equation (6) are more nearly linear than those based on equation (5), but they both lead to the same values of Λ_0. The limiting slopes approached by the more linear plots were used in the estimation of K. The results of the extrapolations are $\Lambda_0 = 132.8$, $K = 0.0049$ for zinc sulfate, and $\Lambda_0 = 133.6$, $K = 0.0043$ for copper sulfate. Davies[17] reported $K = 0.0045$ for both salts at 18°.

To illustrate the dependence of K upon the type of conductance function, the same values of $y_{\text{stoi.}}$ used above, and the equation

$$\Lambda_i = \Lambda_0 - (\alpha\Lambda_0 + \beta)\sqrt{C\vartheta} + BC\vartheta \tag{9}$$

lead to $\Lambda_0 = 132.9$ and $K = 0.0047$ for zinc sulfate when B is 2350. In making this calculation, $\vartheta = \Lambda/\Lambda_i$, and Λ_0 and B are adjusted by trial to yield a constant value of K. In this particular case K showed a total variation of only 0.6% between 0.005 and 0.01 molal. A variation of four or five times this figure would seem permissible in such a determination, and it is interesting to note that within these limits we can obtain values of K as low as 0.0044, and Λ_0 as high as 133.3 for zinc sulfate by means of equation (9).

The Bjerrum equation[14] permits an independent estimate of K from activity coefficient data alone. The substitution of $a = 3.64$ Å. in this equation, with proper attention to valence, leads to $K = 0.0030$ at 25°. The discordance between this value and those derived above from conductivities is not so serious as might appear on first sight, because of the very loose physical sense in which K is defined. Even the difference between the values obtained by equations (6) and (9) shows that K for zinc sulfate is more arbitrary than that for a weak electrolyte such as acetic acid, and leads one to suspect that its present status is more of the nature of an adjustable mathematical parameter than a definite physical entity.[25]

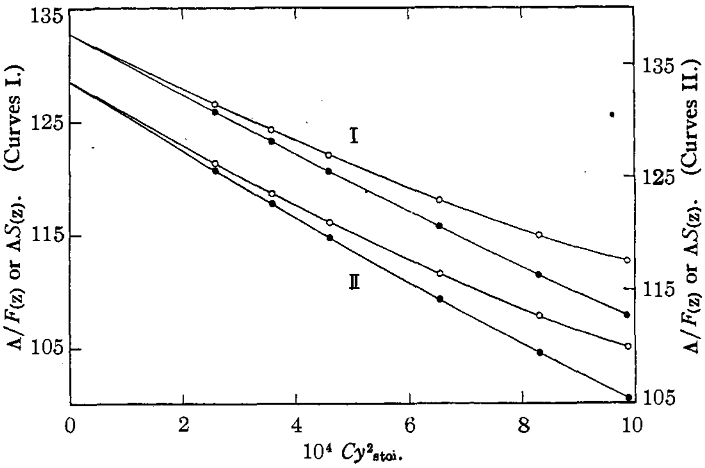

Fig. 1.—Determination of Λ_0 and K for $ZnSO_4$ (Curves I) and $CuSO_4$ (Curves II) at 25°.

In comparing the results of our extrapolations with those available in the literature we find considerable discordance. O'Connor[26] obtained $\Lambda_0 = 142$ for copper sulfate from data extending down to 0.000025 mole per liter, but reports no experimental details. We attempted to extend our measurements to 0.000087 mole per liter with the use of 30,000 ohm shunt, but have not included them in our tabulations because the shunt introduces an error of the order of ± 0.1% in κ and we feel that the pH measurements and solvent corrections are unreliable at such dilutions. It may be significant, however, that our points at $c \simeq 0.000087$ would cause the plots in Fig. 1. to curve

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[21] Bray, THIS JOURNAL, **49**, 2372 (1927).

[22] Cowperthwaite and La Mer, *ibid.*, **53**, 4333 (1931).

[23] Kielland, *ibid.*, **58**, 1855 (1936).

[24] Wetmore and Gordon, *J. Chem. Phys.*, **5**, 60 (1937).

[25] In this connection, *cf.* Cowperthwaite, *Trans. Faraday Soc.*, **29**, 593 (1933).

[26] O'Connor, *Nature*, **139**, 151 (1937).

abruptly upward and increase the intercepts by about one conductance unit.

No recent direct determination of Λ_0 at 25° for zinc sulfate has come to our attention, but Courrell, Hamilton and Butler[27] published data which, according to their observed slopes, would lead to $\Lambda_0 \simeq 125.9$ for zinc chloride or $\lambda_0 \simeq 49.6$ for the zinc ion. Using $\lambda_0 = 79.6$ for the sulfate ion, derived from Shedlovsky's value of Λ_0 for sodium sulfate quoted by Longsworth,[28] our values of λ_0 for the zinc and copper ions would be 53.1 and 53.9, respectively.

Summary

The specific conductivities and *p*H values of dilute zinc and copper sulfate solutions were measured at 25°. The results were corrected for hydrolysis, and the equivalent conductances of the hypothetical unhydrolyzed salts reported at even values of $\sqrt{C}$.

The limiting equivalent conductances and "ionization constants" of the salts were estimated by several procedures based upon the interionic attraction theory and the law of mass action. The dependence of the results upon the nature of the extrapolation function was discussed, and $\Lambda_0 = 132.8$, $K = 0.0049$ for zinc sulfate, and $\Lambda_0 = 133.6$, $K = 0.0043$ for copper sulfate were proposed as the most reliable values.

NEW HAVEN, CONN.

RECEIVED OCTOBER 8, 1938

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[27] Courrell, Hamilton and Butler, *Proc. Roy. Soc.* (London), **A147**, 418 (1934).

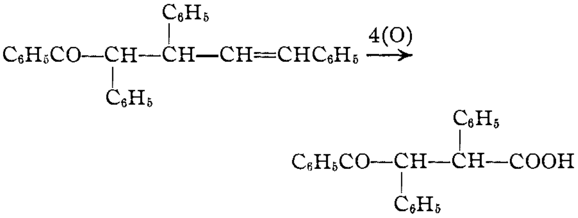
[28] Longsworth, THIS JOURNAL, **57**, 1185 (1935).

[CONTRIBUTION FROM THE SANDERS LABORATORY OF CHEMISTRY, VASSAR COLLEGE, AND THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

α,β-Diphenyl-β-benzoylpropionic Acid

BY H. MARJORIE CRAWFORD

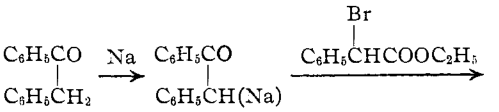
α,β-Diphenyl-β-benzoylpropionic acid has been prepared by Reimer and Reynolds[1] by the oxidation of α,β-diphenyl-γ-benzalbutyrophenone



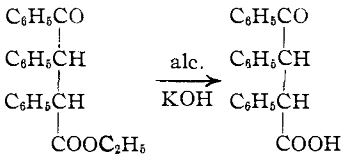
$$C_6H_5CO-\underset{C_6H_5}{CH}-\overset{C_6H_5}{CH}-CH{=}CHC_6H_5 \xrightarrow{4(O)} C_6H_5CO-\underset{C_6H_5}{CH}-\overset{C_6H_5}{CH}-COOH$$

They reported that the acid melted at 211–212° and crystallized from alcohol with one molecule of alcohol of crystallization. They also prepared the methyl ester which melted at 159°.

A simpler method of preparation was sought to obtain considerable quantities of the acid for use in connection with some other work. The following procedure* was adopted

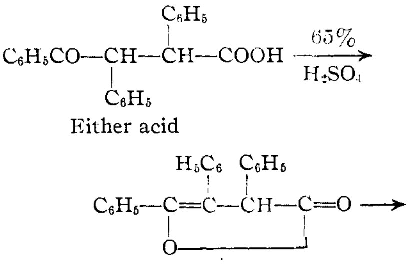


$$\begin{array}{c}C_6H_5CO\\ |\\ C_6H_5CH_2\end{array} \xrightarrow{Na} \begin{array}{c}C_6H_5CO\\ |\\ C_6H_5CH(Na)\end{array} \xrightarrow{C_6H_5\overset{Br}{\overset{|}{C}}HCOOC_2H_5}$$



$$\begin{array}{c}C_6H_5CO\\ |\\ C_6H_5CH\\ |\\ C_6H_5CH\\ |\\ COOC_2H_5\end{array} \xrightarrow[KOH]{alc.} \begin{array}{c}C_6H_5CO\\ |\\ C_6H_5CH\\ |\\ C_6H_5CH\\ |\\ COOH\end{array}$$

Analyses and neutralization equivalent ensured the identity of the product, but it consisted of a mixture of the two racemic modifications of the acid, one melting at 201–202° and the other melting at 211–212°. The high melting isomer yields the 159° methyl ester reported by Reimer and Reynolds. The low melting form was formed in much larger quantities. Treatment of either acid with 65% sulfuric acid gave a lactone which must have the double bond in the β,γ-position since it can be hydrolyzed to give a mixture of both acids



$$C_6H_5CO-\underset{C_6H_5}{CH}-\overset{C_6H_5}{CH}-COOH \xrightarrow[H_2SO_4]{65\%}$$

Either acid

$$C_6H_5-\underset{|}{C}{=}\overset{H_5C_6}{C}-\overset{C_6H_5}{CH}-\underset{|}{C}{=}O \longrightarrow$$

Lactone

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[1] Reimer and Reynolds, *Am. Chem. J.*, **40**, 435 (1908).

* This method of preparation of the acid and other preparations and analytical results marked with an asterisk formed part of the thesis submitted by Brunhilde Reich as partial fulfilment of the requirements for the degree of Master of Arts at Vassar College.