(2) The hydrolysis of the chlorides and nitrates, etc., of calcium, magnesium, strontium and barium employed in the study of this problem, is so small that it alone cannot account for the results obtained.

(3) Salts with water of crystallization increase the velocity of the saponification of an ester to a greater extent than salts with no water of crystallization.

(4) On dilution, the effect with salts having water of crystallization decreases more rapidly than with salts without crystal water, which shows that the result cannot be due to hydrolysis alone.

(5) The curves for the saponification of methyl formate are very similar to those for methyl acetate.

(6) The large effect of salts with water of crystallization is probably due, in part, to their being hydrated, combined water being more highly ionized than free water.

(7) The amount of the saponification, and, therefore, the position of the curve seems to be due to the combined effect of both cation and anion.

(8) It is probable that anions as well as cations are somewhat hydrated.

(9) The hydration of cations is inversely proportional to their atomic volumes.

(10) There seems to be a dilution of maximum saponification for each salt.

(11) Hydrated salts show a large temperature coefficient, notwithstanding the decomposition of hydrates with rise in temperature, probably due in part to hydrolysis.

(12) Decomposition of hydrates may play an important role in the increased velocity of chemical reactions with rise in temperature.

(13) The chemical differences between free and combined water are analogous to the physical differences.

Further work is now in progress in this laboratory on this problem. Certain apparent discrepancies in this preliminary communication are being further investigated, and other lines of attack opened up.

BALTIMORE, MD.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE JOHNS HOPKINS UNIVERSITY.]

CONDUCTIVITIES OF CERTAIN ORGANIC ACIDS IN ABSOLUTE ETHYL ALCOHOL.

BY H. H. LLOYD. JOHN B. WIESEL AND HARRY C. JONES.[1]

Received August 30, 1915.

During the past six years a fairly thorough and systematic study of the conductivity and dissociation of aqueous solutions of organic acids, as

---

[1] The results of this investigation are recorded in full in *Publ. Carnegie Inst. Wash.*, No. 230 (1915).

affected by temperature as well as by dilution, has been in progress in this laboratory.[1] In view of the fact that very little work had been done upon solutions of organic acids in absolute ethyl alcohol, it was decided to extend our investigations into this field.[2] Accordingly Wightman, Wiesel and Jones undertook a preliminary investigation of the problem, worked out a fairly satisfactory method of procedure and made conductivity measurements of nine organic acids.[3] The present investigation is a continuation and extension of their work.

Experimental.

Reagents.—Absolute alcohol was prepared in the manner described by Wightman, Wiesel and Jones.[4] It never contained more than 0.04% water, and its specific conductivity averaged 2×10^{-7}.

The organic acids were obtained from two well-known firms. The same methods of purifying them were employed as when the conductivities of these acids were determined in aqueous solution.[5] After purification they were carefully dried in a vacuum desiccator containing sulfuric acid. Whenever practicable the melting point (of the acids) was taken as one criterion of purity.

Aqueous solutions of ammonia were used for titration purposes, since ammonia had been found by Wightman, Wiesel and Jones[6] to give the most satisfactory results. Corallin (rosolic acid) was used as the indicator, because it is sensitive to ammonia and to organic acids, and is not sensitive to carbon dioxide except when the latter is present in fairly large quantity. The endpoint with corallin is not quite as sharp and distinct as with phenolphthalein, and considerable practice is necessary before reliable results can be obtained.

Apparatus.—On account of the high resistance of the alcoholic solutions of the acids it was found necessary to make use entirely of the cylindrical type of conductivity cell. The method of obtaining the constants of these cells was described by White[7] and by Wightman.[8]

Since the percentage temperature coefficients of conductivity for substances dissolved in alcohol, as well as the coefficient of expansion of the alcohol itself, are so large, it is necessary to regulate the temperature as closely as possible. This was done by the combination of a specially devised gas regulator and thermoregulator. These have already been

---

[1] *Publ. Carnegie Inst. Wash.*, No. 170, Part II (1912); No. 210, Chapter II (1915).

[2] *Am. Chem. J.*, 44, 156 (1910); 46, 56 (1911); 48, 320, 411 (1912); 50, 1 (1913).

[3] THIS JOURNAL, 36, 2243 (1914); *Publ. Carnegie Inst. Wash.*, No. 210, Chapter III (1915).

[4] THIS JOURNAL, 36, 2246 (1914).

[5] *Am. Chem. J.*, 44, 156 (1910); 46, 56 (1911); 48, 320, 411 (1912); 50, 1 (1913).

[6] THIS JOURNAL, 36, 2247–9 (1914).

[7] *Am. Chem. J.*, 42, 527 (1909).

[8] *Ibid.*, 44, 64 (1911).

described in a paper by Davis and Hughes.[1] The constant temperature baths employed were of the improved form designed by Dr. Davis,[2] of this laboratory. In these baths ordinarily the temperature does not vary more than 0.01°, which is sufficiently constant for our purpose. With greater precautions as to insulation against changes in temperature, and with further modification of the thermoregulator, the variation can be decreased to a few thousandths of a degree. The thermometers employed were of the differential Beckmann type, and were carefully compared with a standard Reichsanstalt thermometer, which had been calibrated also at the United States Bureau of Standards. The resistance box which was used throughout this entire investigation had also been calibrated at the Bureau of Standards. A very fine Kohlrausch slide-wire bridge was employed, by means of which it was possible to read distances on the slide-wire corresponding to tenths of a millimeter (the total length of the wire was five meters). Flasks, pipets and burets for measuring purposes were in all cases carefully calibrated.

Procedure.—The solutions of organic acids in alcohol were made up in 200 cc. Jena measuring flasks calibrated for 25°.[3] A portion of each solution was removed to fill the conductivity cells and the remainder was used for the titrations, which were made simultaneously with the conductivity measurements. At first thought it would seem probable that keeping the solutions in the flasks at a constant temperature (25°), and subjecting the solutions in the cells to changes in temperature (15–35°), would produce a change in the rates of esterification. If this were true, the normalities of the solutions in the cells would be different from the values obtained by the titration of the solutions in the flasks, and a considerable error would be introduced. It was found, however, that there was no appreciable difference in the amount of acid present at any moment in a given solution, whether the solution was kept in the 25° bath continuously for 8 hours or whether it was transferred from one bath to another during this time. The reason for this is to be found no doubt in the slow rate at which esterification takes place under the conditions of this investigation.

Although it is fairly certain, then, that variation in the temperature has no measurable effect upon the rate of esterification in alcoholic solutions of the organic acids, this variation does alter to a considerable extent the volume, and therefore the concentration of these solutions. For example, a solution which has a volume of 1000 cc. at 25° contracts to 989.23 cc. when cooled to 15°, and expands to 1011.14 cc. when warmed to 35°. Because of this fact a correction has to be applied to the volume calculated

---

[1] *Z. physik. Chem.*, **85**, 519 (1913).

[2] *Publ. Carnegie Inst. Wash.*, No. **210**, 121 (1915).

[3] Cf. THIS JOURNAL, **36**, 2247 (1914).

from titration, before molecular conductivity can be estimated at 15° and 35°. This correction was made in the following way: Let us suppose that the normality of a given solution at 25°, as determined by titration against ammonia, is N_{25}. The normality at 15°, N_{15}, would then be expressed by the ratio $N_{25}/0.98923$, and the true volume at 15° (*i. e.*, the number of liters which contain a gram molecular weight of the dissolved acid) would be the reciprocal of this ratio, or $0.98923/N_{25}$. Similarly, the normality at 35° would be $N_{25}/1.01114$ and the volume would be $1.01114/N_{25}$.

Results.

In the following tables of conductivity results, V_m is the volume at which the solutions were made up; V_c is the corrected volume. The corrections were applied in the manner just described, both for expansion or contraction of the alcohol and for change in the concentration of the acid due to formation of ester. Molecular conductivity, μ_v, was calculated in the usual manner.

MOLECULAR CONDUCTIVITIES.

Acid.	V_m.	V_c.	μ_v 15°.	V_c.	μ_v 25°.	V_c.	μ_v 35°.
Phenyl acetic	8	7.94	0.004176	8.04	0.005660	8.13	0.007325
	32	32.70	0.01122	33.42	0.01614	34.08	0.02167
	128	146.9	0.04392	152.2	0.06347	156.9	0.08598
	512	537.9	0.1581	545.0	0.2245	552.2	0.2976
Oxyisobutyric	8	7.99	0.005234	8.08	0.006666	8.17	0.008346
	32	32.71	0.01429	33.33	0.01813	33.84	0.02264
	128	139.5	0.05022	143.3	0.06391	147.3	0.07969
	512	537.6	0.1699	543.8	0.2208	550.1	0.2718
Bromo-palmitic	8	7.97	0.007014	8.06	0.009027	8.16	0.01142
	32	33.07	0.01776	33.52	0.02316	33.99	0.02964
	128	151.8	0.07013	154.9	0.09248	158.1	0.1183
	512	540.0	0.2349	546.1	0.3129	552.5	0.3950
Malonic	8	8.12	0.0190	8.13	0.0237	8.18	0.0319
	32	32.9	0.0434	33.2	0.0555	33.7	0.0737
	128	129.3	0.0775	129.5	0.0985	129.6	0.1351
	512	512.8	0.2533	514.9	0.3160	518.1	0.4338
Ethylmalonic	8	7.96	0.01937	8.05	0.02590	8.15	0.03346
	32	32.28	0.06333	32.70	0.08345	33.13	0.1066
	128	134.9	0.2459	137.1	0.3236	140.6	0.4134
	512	532.4	0.9924	538.5	1.295	545.1	1.624
Diethylmalonic	8	7.95	0.02857	8.05	0.03860	8.14	0.05022
	32	32.25	0.06042	32.66	0.08044	33.04	0.1054
	128	136.0	0.1257	139.1	0.1732	142.2	0.2279
	512	533.3	0.2527	539.4	0.3441	546.0	0.4494
Propylmalonic	8	7.95	0.03271	8.04	0.04220	8.13	0.05280
	32	32.21	0.07995	32.63	0.1049	33.09	0.1326
	128	136.0	0.2739	139.1	0.3663	141.4	0.4628
	512	533.3	1.021	539.4	1.346	545.7	1.692

MOLECULAR CONDUCTIVITIES (*continued*).

Acid.	V_m.	V_c.	μ_v 15°.	V_c.	μ_v 25°.	V_c.	μ_v 35°.
Dipropylmalonic	8	8.12	0.03354	8.22	0.04453	8.33	0.05772
	32	31.29	0.06759	31.84	0.09058	32.45	0.1178
	128	130.3	0.1416	131.9	0.1889	133.6	0.2442
	512	540.3	0.3031	548.8	0.4078	558.3	....
Butylmalonic	8	7.97	0.0169	8.08	0.0219	8.19	0.0277
	32	32.89	0.0269	33.65	0.0363	34.26	0.0479
	128	142.3	0.0549	147.8	0.0794	153.2	0.1069
	512	535.0	0.1257	547.6	0.1780	555.0	0.2364
Allylmalonic	8	7.97	0.01309	8.06	0.01757	8.15	0.02304
	32	33.07	0.02867	33.52	0.03882	34.01	0.05068
	128	142.4	0.08701	145.2	0.1170	148.6	0.1491
	512	540.6	0.2822	546.7	0.3756	553.4	0.4798
Benzylmalonic	8	7.95	0.03391	8.04	0.04200	8.13	0.05155
	32	32.23	0.04880	32.64	0.06189	33.04	0.07738
	128	134.7	0.1043	137.1	0.1361	139.4	0.1723
	512	533.0	0.3017	539.1	0.4032	545.7	0.5091
Monobromosuccinic	8	....	....	....	....	....	....
	32	33.02	0.0426	33.65	0.0556	34.26	0.0736
	128	150.1	0.0827	157.1	0.1177	162.5	0.1589
	512	539.1	0.2167	546.4	0.3087	553.4	0.4112
Dibromosuccinic	8	7.96	0.01839	8.06	0.02441	8.16	0.03213
	32	32.31	0.03648	32.76	0.04816	33.15	0.06206
	128	136.4	0.09984	139.1	0.1289	142.2	0.1654
	512	533.3	0.3130	539.4	0.4051	546.0	0.5105
Sebacic	8	8.71	0.001794	8.83	0.002411	8.95	0.003141
	32	34.20	0.004001	34.79	0.005566	35.44	0.007549
	128	138.7	0.01387	140.6	0.01884	142.6	0.02510
	512	579.5	0.04694	593.1	0.06465	605.1	0.08592
Thiodiglycolic	8	8.65	0.02326	8.76	0.02951	8.88	0.03746
	32	33.95	0.03263	34.57	0.04269	35.15	0.05557
	128	138.1	0.05261	140.0	0.07042	141.7	0.09281
	512	568.2	0.1119	579.7	0.1501	587.5	0.2015
Benzilic	8	7.96	0.01660	8.05	0.02200	8.14	0.02799
	32	32.17	0.05527	32.56	0.07267	33.04	0.09271
	128	134.0	0.2176	137.1	0.2882	141.0	0.3711
	512	531.8	0.8849	537.9	....	544.8	1.217
Maleic	8	7.95	0.1504	8.04	0.1922	8.14	0.2400
	32	32.24	0.2913	32.86	0.3768	33.38	0.4736
	128	136.3	0.5977	139.8	0.7806	145.1	1.0034
	512	532.7	1.184	540.5	1.537	546.8	1.932
Fumaric	8	7.98	0.00471	8.09	0.00629	8.19	0.00815
	32	32.66	0.00941	33.20	0.01291	33.79	0.01710
	128	140.3	0.0282	144.8	0.0392	145.8	0.0515
	512	535.0	0.0920	543.2	0.1276	550.4	0.1668

MOLECULAR CONDUCTIVITIES (*continued*).

Acid.	V_m.	V_c.	μ_v 15°.	V_c.	μ_v 25°.	V_c.	μ_v 35°.
Itaconic	8	7.95	0.01452	8.05	0.01946	8.14	0.02504
	32	32.25	0.05870	32.74	0.07795	33.20	0.09963
	128	133.0	0.2413	135.6	0.3214	137.9	0.4100
	512	532.1	0.9737	538.5	1.2762	545.1	1.531
Mesaconic	8	8.11	0.006683	8.22	0.008393	8.36	0.01044
	32	31.67	0.01264	32.47	0.01636	33.16	0.02059
	128	130.5	0.03132	132.6	0.04005	134.6	0.05074
	512	551.1	0.1080	564.3	0.1405	575.5	0.1784
Phenylpropiolic	8	7.95	0.01797	8.04	0.02240	8.13	0.02712
	32	32.23	0.03400	32.61	0.04278	32.99	0.05181
	128	135.3	0.06868	137.5	0.08641	139.8	0.1070
	512	532.4	0.1535	538.8	0.1932	545.1	0.2478
Aconitic	8	7.95	0.01359	8.45	0.01757	8.15	0.02238
	32	33.06	0.02529	33.63	0.03403	34.26	0.04481
	128	150.1	0.06649	155.6	0.09492	164.2	0.1309
	512	539.1	0.1838	545.2	0.2606	551.9	0.3471
Benzoic	8	7.945	0.002892	8.05	0.004073	8.15	0.005444
	32	32.62	0.009884	32.99	0.01405	33.51	0.01893
	128	137.3	0.04311	143.3	0.06205	149.7	0.08563
	512	536.7	0.1583	544.7	0.2233	552.2	0.2960
m-Chlorbenzoic	8	7.94	....	8.04	0.005422	8.15	0.007153
	32	32.84	0.01136	33.40	0.01610	33.79	0.02149
	128	147.8	0.04907	151.7	0.06978	157.4	0.09523
	512	537.9	0.1829	545.0	0.2556	552.2	0.3402
m-Nitrobenzoic	8	7.98	0.005725	8.08	0.007470	8.17	0.009575
	32	32.65	0.01786	33.07	0.02308	33.54	0.02915
	128	140.8	0.07293	143.5	0.09414	146.9	0.1178
	512	537.9	0.2754	544.1	0.3526	550.7	0.4362
1,3,5-Dinitrobenzoic	8	7.95	0.01947	8.04	0.02554	8.13	0.03290
	32	32.28	0.03083	32.72	0.04113	33.15	0.05377
	128	135.6	....	138.7	....	141.4	....
	512	532.7	0.4427	538.8	0.4980	545.1	0.6192
Picric	8	8.69	2.934	8.80	3.502	8.91	4.120
	32	34.02	5.202	34.64	6.264	35.15	7.392
	128	138.3	9.569	140.3	11.445	142.2	13.484
	512	570.8	18.192	585.8	22.031	597.3	26.106
Sulfosalicylic	8	7.97	16.63	8.06	....	8.15	25.63
	32	32.24	26.60	32.68	30.68	33.14	34.87
	128	137.6	36.46	140.7	42.81	143.9	50.06
	512	533.0	40.18	539.4	44.35	546.0	55.94
o-Aminobenzoic	8	7.98	0.03531	8.07	0.04290	8.17	0.05160
	32	32.62	0.02760	33.07	0.03400	33.53	0.04242
	128	139.9	0.05148	142.7	0.06279	145.5	0.07697
	512	534.4	0.1817	540.5	0.2092	546.9	....

MOLECULAR CONDUCTIVITIES (*continued*).

Acid.	V_m.	V_c.	μ_v 15°.	V_c.	μ_v 25°.	V_c.	μ_v 35°.
p-Aminobenzoic	8	7.95	0.2020	8.05	0.2427	8.14	0.2897
	32	32.36	0.2397	32.80	0.2910	33.23	0.3512
	128	138.1	0.2665	141.4	0.3331	143.8	0.4128
	512	533.3	0.2165	539.7	0.2672	545.7	0.3231
o-Toluic	8	7.98	0.005429	8.08	0.006721	8.17	0.008174
	32	32.63	0.01299	33.07	0.01637	33.48	0.01992
	128	140.0	0.04298	142.7	0.05680	144.7	0.06917
	512	537.3	0.1230	543.5	0.1745	549.8	0.2078
p-Toluic	8	7.95	0.001288	8.04	0.001648	8.13	0.002163
	32	32.27	0.003453	32.68	0.004444	33.09	0.005923
	128	136.0	0.01387	138.3	0.01770	141.4	0.02588
	512	532.7	0.04262	539.1	0.05283	545.7	0.06930
Cinnamic	8	7.97	0.001370	8.06	0.001782	8.16	0.002350
	32	32.81	0.003612	33.28	0.004603	33.85	0.006222
	128	141.6	0.01297	144.0	0.01660	146.9	0.02205
	512	535.1	0.04243	541.4	0.04737	548.3	0.06585
Phthalic	8	7.95	0.02880	8.04	0.03945	8.14	0.05217
	32	32.23	0.07932	32.63	0.1077	33.02	0.1401
	128	136.4	0.2804	138.7	0.3771	141.8	0.4847
	512	533.6	1.043	539.7	1.378	546.3	1.747
Dichlorophthalic	8	..	....	..	....	..	....
	32	33.73	0.05056	34.32	0.06579	34.99	0.08331
	128	138.1	0.08203	139.8	0.1047	141.4	0.1315
	512	568.2	0.1386	579.7	0.1803	588.6	0.2313
Anisic	8	7.97	0.01259	8.06	0.01662	8.15	0.02118
	32	..	....	..	....	..	....
	128	142.0	0.2173	144.8	0.2880	146.9	0.3625
	512	539.7	0.8025	545.8	1.052	552.2	1.255
Mandelic	8	8.10	0.005370	8.20	0.007273	8.30	0.009553
	32	32.60	0.01232	33.01	0.01680	33.57	0.02216
	128	129.2	0.03256	130.8	0.04303	132.6	0.05529
	512	455.2	0.09377	498.0	0.1389	504.8	0.1787
Camphoric	16	15.91	0.006475	16.11	0.008957	16.32	0.01138
	64	64.49	0.01058	65.79	0.01539	66.92	0.01907
	256	272.1	0.02258	291.5	0.03236	309.4	0.04301
	1024	1159.0	0.04637	1176.0	0.06706	1191.0	0.09171

Discussion of the Results.

The most striking feature of the conductivities of the organic acids in alcohol, as shown by an examination of the foregoing tables, is their *extremely small value*. In nearly all cases, the conductivities are several hundred times smaller than the conductivities of the same acids in water. When we consider the fact that alcohol has from one-fourth to one-fifth the dissociating power of water, as shown by the dissociation of strong electrolytes in these solvents, the above fact does not at present seem to admit of any very satisfactory explanation.

The effect of increase in the dilution is to increase the molecular conductivity. The increase in conductivity in many cases is almost proportional to the volume.

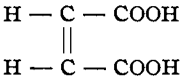
A knowledge of the extent to which organic acids are dissociated in alcoholic solution would be highly desirable. It is hoped that a method for the determination of percentage dissociation will be worked out in the near future. Goldschmidt[1] obtained values for the limiting conductivities of several organic acids in alcohol from the μ_∞ values of their sodium salts. These varied from 83 to 93, depending on the nature of the acid. It has not yet been found practicable to determine the limiting conductivities of the organic acids studied in this investigation, but as a result of Goldschmidt's work it is certain that they do not differ greatly from 90. If this be the case, the dissociation of the organic acids studied by the authors, as determined by conductivity, do not, in any case, exceed 2% even in $N/512$ solutions.

Relation between Composition and Conductivity.

In his classical study of the conductivity of aqueous solutions of organic acids, to which reference has already been made, Ostwald[2] pointed out a number of relations between composition and molecular conductivity. The general validity of these relations has been confirmed by the work which has been in progress in this laboratory for the past fifteen years. In view of this, an examination of the results obtained for alcoholic solutions, in the attempt to discover similar relations, should prove to be interesting.

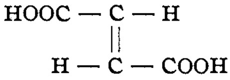
Take the following compounds:

Maleic acid



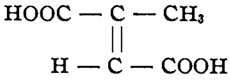
$$\begin{array}{l} \mathrm{H - C - COOH} \\ \quad\ \ \| \\ \mathrm{H - C - COOH} \end{array}$$

Fumaric acid



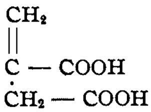
$$\begin{array}{l} \mathrm{HOOC - C - H} \\ \qquad\qquad\ \| \\ \qquad\ \mathrm{H - C - COOH} \end{array}$$

Mesaconic acid



$$\begin{array}{l} \mathrm{HOOC - C - CH_3} \\ \qquad\qquad\ \| \\ \qquad\ \mathrm{H - C - COOH} \end{array}$$

Itaconic acid



$$\begin{array}{l} \mathrm{CH_2} \\ \| \\ \mathrm{C - COOH} \\ \mathrm{CH_2 - COOH} \end{array}$$

The conductivity of maleic acid is many times that of fumaric. This

---

[1] *Z. Elektrochem.*, **15**, 4 (1909); **20**, 473 (1914); *Z. physik. Chem.*, **70**, 627 (1910); **81**, 30 (1912); **89**, 129 (1914).

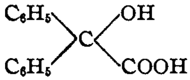
[2] *Z. physik. Chem.*, **3**, 170, 241, 369 (1889).

fact is in keeping with the results obtained in aqueous solution,[1] and with the present-day conception of the configuration of these acids. Mesaconic acid is a methyl substitution product of fumaric acid, and its conductivity is of the same order of magnitude as that of the fumaric acid. Itaconic acid, which is isomeric with mesaconic, but which has very different constitution, shows much higher conductivity. Malonic acid, at a volume at 32 and at 25°, has a molecular conductivity of 0.055. Under the same conditions, ethylmalonic acid has a conductivity of 0.083; diethylmalonic, 0.080; propylmalonic, 0.105; dipropylmalonic, 0.090; butylmalonic, 0.036; allylmalonic, 0.039; and benzylmalonic, 0.062.

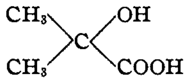
The above results show that the introduction of an ethyl group increases the conductivity, while the introduction of a second ethyl group tends to decrease the conductivity of ethylmalonic acid. Propylmalonic acid has uniformly higher conductivity than ethylmalonic, and the conductivity of the dipropyl acid is uniformly higher than that of the diethyl. Just as diethylmalonic acid has smaller conductivity than ethylmalonic, so, dipropylmalonic acid has smaller conductivity than propylmalonic.

Butylmalonic acid and allylmalonic acid, at the dilution in question, have smaller conductivities than malonic acid itself; but as the dilution increases, the conductivity of allylmalonic acid becomes greater than that of malonic acid.

Benzylmalonic acid has greater conductivity than malonic acid, but less than ethylmalonic acid. This is especially interesting, in consideration of the fact that, in general, a phenyl derivative of an acid has much greater conductivity than the corresponding methyl derivative; *e. g.*, the conductivity of acetic acid in alcohol is so small that it cannot be accurately measured. On the other hand, benzoic acid has a conductivity of 0.014. Again, benzilic acid having the formula



has a much greater conductivity than the corresponding methyl derivative, oxyisobutyric acid



This is in keeping with the results obtained for these acids in aqueous solution,[2] and with the general observation that the replacement of a methyl group by a phenyl group increases the conductivity.

Phenylpropiolic acid $C_6H_5 - C \equiv C - COOH$ has a conductivity many times larger than that of cinnamic acid

---

[1] *Publ. Carnegie Inst. Wash.*, No. 170, 113 (1912).

[2] *Ibid.*, No. 170, 115, 132 (1912).

$$C_6H_5 — CH = CH — COOH.$$

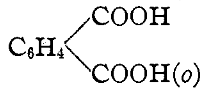
This is in accord with what was found for these same acids in aqueous solutions.

Take the following series:

Benzoic acid,	C_6H_5COOH.
m-Chlorobenzoic acid,	$C_6H_4ClCOOH$.
m-Nitrobenzoic acid,	$C_6H_4NO_2COOH$.
1,3,5-Dinitrobenzoic acid,	$C_6H_3(NO_2)_2COOH$.
o-Toluic acid,	$C_6H_4CH_3COOH$.
p-Toluic acid,	$C_6H_4CH_3COOH$.

The conductivities of benzoic acid and of *o*-toluic acid are about equal, whereas the conductivity of *p*-toluic acid is very much less. That the same relation holds also for other substituent groups may be seen from the results obtained a year ago by Wightman, Wiesel and Jones.[1] For example, the conductivity of *o*-chlorobenzoic acid and of *o*-nitrobenzoic acid are approximately the same as that of benzoic, but the conductivities of the corresponding para-acids are considerably less.

It is a well established fact that in aqueous solution the conductivity of benzoic acid is somewhat increased by the introduction of methyl, chlorine, or the nitro group, in the para position; and enormously increased by the introduction of one of these groups in the ortho position. In contradistinction to this, the effect of these groups upon the conductivity in alcoholic solution appears to be negative. Just the opposite is true if the chlorine or nitro group occupies the meta position. In these cases the conductivity of benzoic acid is somewhat increased.

The introduction of a second nitro group into *m*-nitrobenzoic acid still further increases the conductivity. While benzoic acid C_6H_5COOH has a conductivity of only 0.015, phthalic acid  $C_6H_4\begin{cases}COOH\\COOH(o)\end{cases}$ a dicarboxy derivative, has a conductivity of 0.108, which is seven times as great. This same relation holds in aqueous solutions.[2]

Of all the acids studied in this investigation, with one exception, picric acid, $C_6H_2(NO_2)_3OH$ is the strongest. The only stronger acid in alcoholic solutions is sulfosalicylic, which has a conductivity approaching that of hydrochloric acid in this solvent. This is in general analogous to what was found when these compounds were dissolved in water,[3] sulfosalicylic acid in water having almost exactly the same conductivity as hydrochloric acid in that solvent.

In order to compare the conductivities of the above named organic

---

[1] THIS JOURNAL, 36, 2251–2252 (1914).

[2] *Publ. Carnegie Inst. Wash.*, No. 170, 116, 133 (1912).

[3] *Ibid.*, 170, 120, 121 (1912).

acids in alcohol, with the conductivities of these same compounds in water, reference must be had to *Publication of the Carnegie Institution of Washington*, No. 170 (1912).

BALTIMORE, MD.

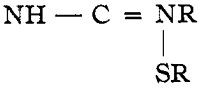
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF KANSAS.]

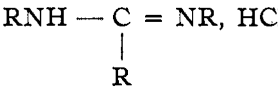
ON THE ACTION OF CERTAIN ACID REAGENTS ON THE SUBSTITUTED UREAS AND THIAZOLE.

[SECOND PAPER.]

BY F. B. DAINS, R. C. ROBERTS AND R. Q. BREWSTER.

Received November 13, 1915.

This is a continuation of an investigation[1] begun several years ago on the reactivity of the anilido hydrogen in the oxygen and sulfur ureas and is a study of the effect of acyl reagents on the grouping —NHCO(S)NH— or  $NH - \underset{SR}{\underset{|}{C}} = NR$ in both open-chain and ring compounds.

Disubstituted Ureas and Acid Chlorides.—As has been previously shown, a urea of the type RNHCONHR reacts with an acid chloride at 150–160° giving the amidine hydrochloride,  $RNH - \underset{R}{\underset{|}{C}} = NR, HCl$ and carbon dioxide. An acyl derivative of the urea is first formed. This then dissociates into carbanilide and an isocyanate, RNHCOR + RNCO, which at the temperature employed react giving carbon dioxide and the amidine.[2]

Molecular proportions of benzoyl chloride and di-*o*-tolylurea were heated in a sealed tube at 170° for four hours. The tube opened with pressure, due to carbon dioxide and hydrogen chloride, while the odor of isocyanate could be detected in the escaping gases. The solid contents of the tube consisted of benz-*o*-toluide and the hydrogen chloride salt of a base, which was freely soluble in water. The base, benz-di-*o*-tolylamidine, $C_6H_5 - C = NC_7H_7(NHC_7H_7)$ was precipitated with sodium hydroxide and purified by crystallization from alcohol, in which it is easily soluble. It separated in fine, white needles melting at 87–8°.

Calc. for $C_{21}H_{20}N_2$: N, 9.33%. Found: 9.44%.

Diphenylurea and isovaleryl chloride react at 140° giving a base, isovaler-diphenylamidine, which melts at 103°. It was identified by the analysis of the yellow platinum salt, which has a melting point of 207°.

Calc. for $(C_{17}H_{20}N_2)_2H_2PtCl_6$: Pt, 21.35%. Found: 21.22%, 21.44%.

---

[1] THIS JOURNAL, **22**, 181 (1900).

[2] *Ibid.*, **22**, 188 (1900).