

**1,1'-Ethyneylene-bis-3,4-dihydronaphthalene.**—Treatment of the acetylenedimagnesium bromide prepared from 15.3 g. of magnesium, 65.5 g. of ethyl bromide and acetylene in 350 cc. of ether with 86 g. of  $\alpha$ -tetralone in 150 cc. of ether gave 22 g. of a crude product which after crystallization from benzene melted at 120–121°. Analysis indicated that it was not the expected glycol but its dehydration product.

*Anal.* Calcd. for  $C_{22}H_{18}$ : C, 93.58; H, 6.42. Found: C, 93.68; H, 6.53.

Attempts to cyclize this product with the usual reagents gave amorphous products.

**1,6-Diphenyl-2,5-diisobutyl-1,5-hexadiene-3-yne.**—Eighty-eight grams of benzyl isobutyl ketone was treated with acetylenedimagnesium bromide in the usual fashion to give 29 g. of a crude glycol which was not purified but was dehydrated directly by heating with potassium bisulfate. There was thus obtained 19 g. of the expected diene-yne; b. p. 160–190° at 2 mm. Redistillation gave a viscous product; b. p. 179–180° at 2 mm.;  $n_D^{20}$  1.5872;  $d_4^{20}$  0.9951.

*Anal.* Calcd. for  $C_{26}H_{30}$ : C, 91.17; H, 8.83. Found: C, 90.28; H, 8.93.

Attempts to cyclize this diene-yne by treatment with sulfuric and acetic acids or formic acid were unsuccessful. Most of the diene-yne was recovered, but it was contaminated with a bluish, volatile product which was destroyed gradually by several distillations.

### Summary

1. Di- $\Delta^1$ -cyclopentenylacetylene could not be cyclized directly to a decahydroketoindacene but by cyclization in a reducing mixture some of the corresponding cyclic hydrocarbon was obtained.

2. Attempts to obtain decahydrochrysene from the condensation product of  $\alpha$ -tetralone and 1-ethynylcyclohexanol-1 led to compounds of doubtful structures.

3. Some limitations to this method of preparing polynuclear compounds have been described.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WASHINGTON]

## The Ionization Constant of Lactic Acid, 0–50°, from Conductance Measurements

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To test the results of a preliminary study made in this Laboratory on the ionization constant of lactic acid, it seemed advisable to determine this important constant from conductance measurements. Because of the importance of lactic acid in biochemical reactions an accurate knowledge of its physicochemical constants is of considerable significance. Before the completion of this investigation Nims and Smith<sup>1</sup> reported results on the ionization constant of lactic acid, 0–50°, from electromotive force measurements.

Results of the present investigation are from conductance measurements. The method used was, with certain minor changes, essentially the procedure used by MacInnes and Shedlovsky<sup>2</sup> in the determination of the ionization constant of acetic acid combined with the procedure of these same workers<sup>3</sup> in extending conductance measurements, in the determination of the ionization constant of carbonic acid, to a range of temperature.

**Apparatus.**—It was necessary in this investigation to use different conductance assemblies. Both a Leeds and Northrup conductivity bridge<sup>4</sup> and a conductivity bridge

constructed according to specifications given by Jones and Josephs<sup>5</sup> were used. It was possible, however, by using the same conductance cell and a temperature of 25° to compare resistance measurements of the bridges. Comparison of the bridges was within the limits of accuracy with which measurements could be carried out using a single assembly. The conductance cell, used with nitrogen, was similar in design to a cell described by Shedlovsky.<sup>6</sup> Because of the magnified effects of adsorption at very dilute concentrations it was desirable to limit platinization to the minimum value allowed by polarization. For measurements included in this investigation the electrodes of the conductance cell were given a light gray coating of platinum using the procedure suggested by Jones and Bollinger.<sup>7</sup> The cell constant at 25° was of the order of 0.37252. The oscillators were similar to one described by Jones and Josephs.<sup>5</sup> A two-stage vacuum tube amplifier was used. The oil thermostat varied by not more than 0.005° from the temperature established by a thermometer certified by the Bureau of Standards.

**Materials.**—All solutions were made by weight using weights which had been calibrated and compared with a set certified by the Bureau of Standards. The hydrochloric acid used for standardization of sodium or potassium hydroxide was a carefully prepared constant boiling mixture using the data of Foulk and Hollingsworth.<sup>8</sup> Conductivity water, from a special still, not exceeding a specific conductance of  $4.0 \times 10^{-7}$  was used in the prepara-

(1) Nims and Smith, *J. Biol. Chem.*, **113**, 145 (1936).

(2) MacInnes and Shedlovsky, *THIS JOURNAL*, **54**, 1429 (1932).

(3) Shedlovsky and MacInnes, *ibid.*, **57**, 1705 (1935).

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

(5) Jones and Josephs, *THIS JOURNAL*, **50**, 1049 (1928).

(6) Shedlovsky, *ibid.*, **54**, 1411 (1932).

(7) Jones and Bollinger, *ibid.*, **53**, 411 (1931).

(8) Foulk and Hollingsworth, *ibid.*, **46**, 1220 (1923).

TABLE I

EQUIVALENT CONDUCTANCE OF POTASSIUM LACTATE AT 25°

Concn. $c \times 10^3$ $c = \text{normality}$	Equivalent conductance $\Lambda$ , mhos	Concn. $c \times 10^3$ $c = \text{normality}$	Equivalent conductance $\Lambda$ , mhos
0.0580	111.6	2.928	107.9
.0926	111.4	3.734	107.4
.1805	111.1	3.824	107.1
.2403	111.0	4.283	107.1
.3675	110.8	4.939	106.7
.4080	110.6	6.152	106.1
.4350	110.5	6.901	106.1
.7377	110.0	7.610	105.5
.8742	109.8	7.894	105.4
.9491	109.7	9.259	104.8
1.105	109.7	11.13	104.5
1.252	109.5	14.03	103.4
1.529	109.0	14.58	103.2
1.797	109.4	17.71	102.2
1.917	108.7	21.87	101.5
1.924	108.7	23.06	101.4
2.014	108.6	28.78	100.3
2.647	108.0	30.04	100.2

$\Lambda_0 = 112.27 \quad B = 92.2$

TABLE II

EQUIVALENT CONDUCTANCE OF SODIUM LACTATE AT 25°

Concn. $c \times 10^3$	Equivalent conductance $\Lambda$ , mhos	Concn. $c \times 10^3$	Equivalent conductance $\Lambda$ , mhos
0.1539	87.89	5.902	83.23
.2281	87.68	7.495	82.60
.3472	87.44	8.174	82.33
.6302	86.91	9.475	81.88
.9983	86.43	10.10	81.44
1.622	85.80	11.76	81.18
2.219	85.29	13.06	80.81
2.829	84.87	15.00	80.34
3.629	84.27	19.82	79.27
4.762	83.78	22.61	78.71

$\Lambda_0 = 88.86 \quad B = 85.0$

form of Onsager's equation as developed by Shedlovsky<sup>10</sup> reduces to

$\Lambda_{KLa_0} = 112.27 - 85.32 \sqrt{C} + 92.2 C (1 - \alpha \sqrt{C})$

and for sodium lactate

$\Lambda_{NaLa_0} = 88.86 - 80.01 \sqrt{C} + 85.0 C (1 - \alpha \sqrt{C})$

From the expression

$\Lambda_{eHLac} = \Lambda_{HCl} - \Lambda_{KCl} + \Lambda_{KLa_0}$

and using values of  $\Lambda_{HCl}$  and  $\Lambda_{KCl}$  given by Shedlovsky<sup>6</sup> the value of  $\Lambda_{eHLac}$  from potassium lactate is given by the equation

$\Lambda_{eHLac} = 388.49 - 148.17 \sqrt{C} + 162.8 C (1 - \alpha \sqrt{C})$

tion and dilution of solutions. Potassium chloride used for cell constant determinations was a 0.01 demal solution of the specially purified salt and the value of its specific conductance was that given by Jones and Bradshaw.<sup>9</sup>

Lactic acid was from two sources of the best obtainable analytical reagent. It was further purified by changing to zinc lactate, crystallizing the salt, and decomposing with hydrogen sulfide. The zinc sulfide was allowed to settle and the supernatant liquid was evaporated at low temperature under diminished pressure. The concentrated solution was subjected to three distillations *in vacuo*. In all cases when preparing dilute solutions for use in conductance measurements the acid was distilled *in vacuo* immediately before making conductance measurements.

Concentrations of stock solutions were determined by means of potentiometric titrations in a closed system. Sodium or potassium lactate was prepared by almost neutralizing (to a pH of 6.8) lactic acid with standard hydroxide. It was necessary to know the pH, measured electrometrically, of the lactate in order to make the proper correction for the trace of lactic acid, a procedure<sup>8</sup> adopted to control hydrolysis.

Determination of the ionization constant at 25° involves the determination of the  $\Lambda_0$  value of lactic acid. To determine the limiting equivalent conductance of lactic acid both potassium and sodium lactates were used. Equivalent conductances of potassium and sodium lactates over a limited concentration range are given in Tables I and II and presented graphically in Fig. 1.

The equation expressing the equivalent conductance for potassium lactate using the modified

Likewise

$\Lambda_{eHLac} = \Lambda_{HCl} - \Lambda_{NaCl} + \Lambda_{NaLa_0}$

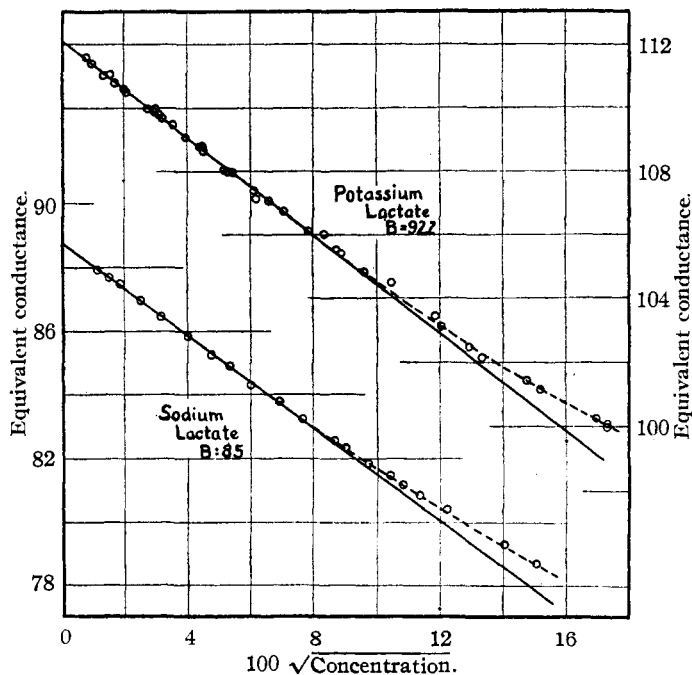


Fig. 1.—Equivalent conductance of potassium lactate and sodium lactate at 25°.

(9) Jones and Bradshaw, THIS JOURNAL, 55, 1780 (1933).

(10) Shedlovsky, *ibid.*, 54, 1405 (1932).

TABLE III  
EQUIVALENT CONDUCTANCE AND IONIZATION CONSTANT OF  
LACTIC ACID AT 25°

Concn. $c \times 10^3$	Ion concn. $a \times 10^3$	Equivalent conductance $\Lambda$ , mhos	Ionization const. $K \times 10^4$
0.1606	0.0960	231.2	1.391
.3817	.1727	175.0	1.385
.5879	.2276	149.6	1.388
.9213	.3005	125.9	1.397
1.076	.3285	118.0	1.385
1.248	.3603	111.4	1.396
1.550	.4074	101.4	1.386
1.689	.4283	97.99	1.387
2.001	.4721	90.91	1.385
2.406	.5569	83.21	1.385
3.216	.6163	73.75	1.378
3.543	.6515	70.70	1.383
4.231	.7179	65.27	1.378
4.732	.7631	62.01	1.376
5.211	.8062	59.47	1.381
5.689	.8424	56.91	1.369
6.196	.8832	54.77	1.370
6.372	.8964	51.61	1.369
7.409	.9708	50.32	1.365
8.266	1.033	47.96	1.368
8.537	1.049	47.16	1.362
9.564	1.116	44.79	1.365
10.69	1.187	42.61	1.369
11.24	1.219	41.60	1.367
12.47	1.287	39.58	1.363
13.62	1.350	37.99	1.363
15.99	1.467	35.24	1.356
17.56	1.548	33.74	1.363
20.85	1.690	31.03	1.354
24.04	1.827	29.05	1.360
27.30	1.951	27.31	1.354
29.82	2.040	26.15	1.349
32.83	2.142	24.92	1.342
37.44	2.292	23.38	1.337
43.05	2.468	21.87	1.337
63.38	2.987	17.95	1.300

which reduces to

$$\Lambda_{\text{HLac}} = 388.48 - 148.18 \sqrt{C} + 161.0 C(1 - \alpha \sqrt{C})$$

using the value for  $\Lambda_{\text{NaCl}}$  given by Shedlovsky.<sup>6</sup>

Equivalent conductance values of lactic acid at 25° over the concentration range indicated together with the thermodynamic ionization constant are given in Table III.

At temperatures other than 25° measurements were made using 0.001 *N* solutions of potassium lactate, lactic acid, potassium chloride and hydrochloric acid. From conductance measurements of the solutions at the temperatures indicated and the relation<sup>3</sup>

$$\frac{K_t}{K_{25}} = \left[ \frac{\Lambda_{\text{ct}}/\Lambda_{\text{ct}}}{\Lambda_{\text{c25}}/\Lambda_{\text{c25}}} \right]^2 \frac{C_t f_t^2}{C_{25} f_{25}^2} \left[ \frac{1 - \Lambda_{\text{c25}}/\Lambda_{\text{c25}}}{1 - \Lambda_{\text{ct}}/\Lambda_{\text{ct}}} \right]$$

the thermodynamic ionization constant of lactic acid was determined, Table IV.

Figure 2 is a graph showing the relationship between  $pK$  ( $-\log K$ ) values and temperature. It is observed that the ionization constant has a maximum value of  $1.389 \times 10^{-4}$  at 22.5°. Included in Fig. 2 are the reported values of Nims and Smith.<sup>1</sup> As can be seen from this figure, the numerous data of Nims and Smith and the single observations of Larsson and Adell, of Ostwald and of Böeseken and others, are in reasonable agreement with our results, although in general somewhat larger. The observations of other investigators are scattered and discordant.

The limiting factor in the determination of the values of  $K$  was the exactness with which the concentrations could be determined, which was of the order of 0.5%. It was observed that dilute solutions of the lactic acid showed a small increase

TABLE IV  
IONIZATION CONSTANT AND CHANGE IN FREE ENERGY, HEAT CONTENT AND ENTROPY ACCOMPANYING THE IONIZATION OF  
LACTIC ACID AT DIFFERENT TEMPERATURES

Temp.	$\Lambda$ , mhos	$\Lambda_e$ , mhos	$\Lambda_0$ , mhos	$K \times 10^4$	$\Delta F^\circ$ , cal.	$\Delta H^\circ$ , cal.	$\Delta S^\circ$ , cal./deg.
0	73.93	240.4	241.9	1.317	4847	768	-14.94
5	82.73	267.1	268.8	1.339	4927	619	-15.49
10	92.25	296.3	298.2	1.356	5008	458	-16.07
15	102.4	326.8	328.9	1.375	5089	285	-16.67
20	111.7	355.0	357.3	1.389	5173	98.2	-17.31
22	115.4	366.7	369.2	1.389	5207	19.9	-17.58
23	117.5	373.3	375.9	1.389	5224	-20.1	-17.71
24	119.4	379.0	381.6	1.389	5242	-60.6	-17.85
25	121.4	385.9	388.5	1.387	5260	-102	-17.99
30	129.7	412.9	415.8	1.378	5352	-315	-18.70
35	137.4	439.5	442.7	1.359	5449	-543	-19.45
38	141.7	454.5	457.8	1.348	5508	-686	-19.91
40	144.6	464.6	468.0	1.339	5547	-785	-20.22
45	150.8	488.5	492.1	1.309	5650	-1041	-21.03
50	157.0	513.4	517.4	1.274	5756	-1313	-21.88

in the measured resistance after standing for several days. All solutions were protected carefully from the atmosphere, being handled in an atmosphere of nitrogen. Precautions were taken to have sterile conditions; for values in this report measurements were on freshly prepared solutions of the lactic acid.

From Table III, up to a concentration somewhere in the neighborhood of 0.005 *N*, values of *K* vary but slightly; however, there is a tendency for the constant to decrease as the concentration of the lactic acid increases. This decrease is expected due to the assumption made that the activity of the undissociated acid is unity, and also due to the fact that in using the Debye-Hückel limiting equation the assumption is made that this equation is valid for the ion concentrations computed, which is true only to a limited extent, as shown by MacInnes and Shedlovsky.<sup>2</sup>

The equation expressing the variation of the ionization constant with temperature is, *t* being °C.

$$pK = 3.857 + 5 \times 10^{-5} (t - 22.5)^2$$

which is the form of equation suggested by Harned and Embree<sup>11</sup> for weak acids.

The change in heat content,  $\Delta H^0$ , for the ionization process is given by the expression

$$\Delta H^0 = -2.303 \times 10^{-4} (t - 22.5) RT^2$$

Included in Table IV are also values for the change in heat content,  $\Delta H^0$ , free energy increase,  $\Delta F^0$ , and entropy,  $\Delta S^0$ , due to the ionization process as calculated from the usual thermodynamic relations.

### Summary

1. The conductances of sodium and potassium lactate, and of lactic acid, have been measured over a wide concentration range at 25° and at a

(11) Harned and Embree, *THIS JOURNAL*, **56**, 1050 (1934).

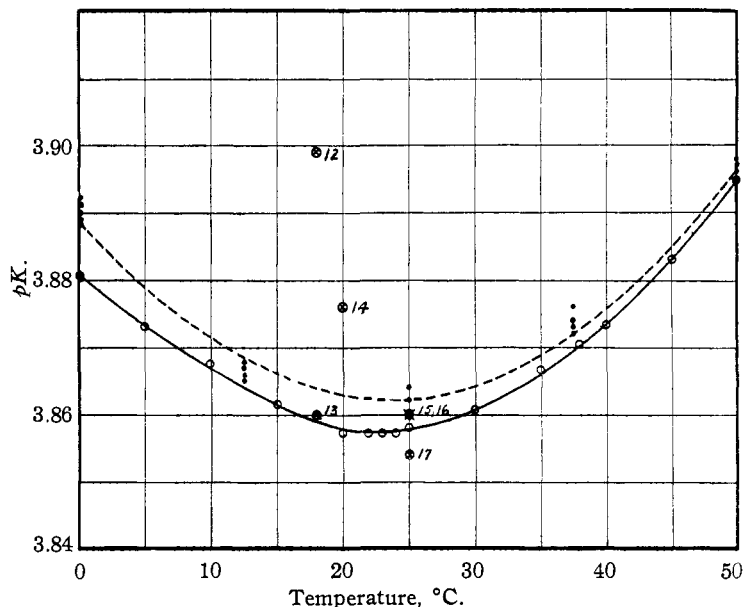


Fig. 2.—*pK* values as a function of temperature: ○ represent values from conductance data; ● and broken line represent data reported by Nims and Smith;<sup>1</sup> ⊗ refer to values of other investigators, numbers opposite are references.

single concentration at temperatures from 0 to 50°; empirical equations expressing these conductances in terms of concentration have been derived.

2. From these measurements the ionization constant of lactic acid at 25° has been calculated and found to be nearly constant over a considerable range with a trend to lower values at high concentration. The ionization constant of lactic acid and the changes in free energy, heat content and entropy accompanying the ionization of this substance from 0 to 50° have also been computed. Empirical equations have been derived for the ionization constant and the change in heat content as functions of the temperature.

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(12) Dietzel and Rosenbaum, *Z. Elektrochem. angew. chem.*, **33**, 196 (1927).

(13) Larsson and Adell, *Z. physik. Chem.*, **A157**, 342 (1931).

(14) Auerbach and Smolczyk, *ibid.*, **110**, 65 (1924).

(15) Böeseken, Hansen and Bertram, *Rec. trav. chim.*, **85**, 309 (1915); *C. A.*, **11**, 38 (1917).

(16) Ostwald, *Z. physik. Chem.*, **3**, 170 (1889).

(17) Magnanini, *Gazz. chim. ital.*, **21**, Pt. II, 215 (1891).