A stirred solution of I (0.85 g.) in 35 ml. of dioxane, 10 ml. of ether, 6 ml. of absolute alcohol and 150 ml. of liquid ammonia was treated portionwise with 1 g. of lithium metal. The mixture was stirred at room temperature for two hours when the excess ammonia had spontaneously evaporated. Extraction with ethyl acetate and evaporation *in vacuo* afforded about 900 mg. of white powder, m.p. 288–291°. The crude product was treated with 40 ml. of acetone, cooled and practically pure *II* was collected; wt. 700 mg., m.p. 297–298°, yield, 82%.

A 70-mg. sample recrystallized from methanol–acetone afforded 50 mg. of pure II, m.p. 300–301°. Admixture m.p. determination with an authentic sample[1] showed no depression; $[\alpha]^{26}\mathrm{D}$ −36° (19.3 mg., pyridine, $\alpha\mathrm{D}$ −0.35°).

11-*epi*-Hydrocortisone.—Compound II (0.4 g., m.p. 297–298°) in 30 ml. of methanol and 4 ml. of 8% (v./v.) sulfuric acid was hydrolyzed in the manner previously described.[1] This gave 193 mg. (60% yield) of pure 11-*epi*-hydrocortisone (recrystallized from acetone–petroleum ether, b.p. 64–66°), m.p. 214–216°, $[\alpha]^{25}\mathrm{D}$ +116° (20.1 mg., absolute alcohol, $\alpha\mathrm{D}$ +1.16°), $\lambda_{\max.}^{\text{abs. alc.}}$ 241–242 mμ, ε 14,800. Admixture m.p. determination, and absorption analysis (infrared, and sulfuric acid chromogen spectra) showed identity with an authentic sample.[1]

Diethylene Ketal of Adrenosterone (Δ^5-Androstene-3,11,-17-trione-3,17-diethylene Ketal).[9] **A.**—Adrenosterone[10] [$\lambda_{\max}^{\text{nujol}}$ 1730 cm.$^{-1}$ (17-keto), 1695 cm.$^{-1}$ (11-keto), 1660 cm.$^{-1}$ (3-keto), 1600 cm.$^{-1}$ (Δ^4), 1258 cm.$^{-1}$ (weak absorption), no hydroxyl absorption][11] (0.3 g.) in 25 ml. of benzene was treated with 2.2 ml. of ethylene glycol and 9 mg. of *p*-toluenesulfonic acid monohydrate in the manner previously described[12] (reflux, 5.5 hours). The crude product was recrystallized from ether, and ether–petroleum ether (64–66°); wt. 0.12 g., m.p. 184.5–185.5°, $\lambda_{\max}^{\text{abs. alc.}}$ none; $\lambda_{\max}^{\text{nujol}}$ 1695 cm.$^{-1}$ (11-keto), 1262 cm.$^{-1}$ (weak absorption), no hydroxyl absorption; $[\alpha]^{29}\mathrm{D}$ −41° (13.5 mg., chloroform, $\alpha\mathrm{D}$ −0.28°).

Anal.[13] Calcd. for $C_{23}H_{32}O_5$ (388.49): C, 71.10; H, 8.30. Found: C, 70.84; H, 8.28.

B.—In another run with 1 g. of adrenosterone, 50 ml. of benzene, 8 ml. of ethylene glycol and 30 mg. of *p*-toluenesulfonic acid monohydrate (reflux, 6 hours), there was obtained 0.93 g. (72%), m.p. 182–184°.

Δ^5-Androstene-11α-ol-3,17-dione-3,17-di-ethylene Ketal.—The diketal of adrenosterone (0.68 g.) in 25 ml. of dioxane, 5 ml. of absolute alcohol and 140 ml. of liquid ammonia was treated with about 1 g. of lithium in the manner described above. Evaporation *in vacuo* of the ethyl acetate extract afforded 0.67 g. of a white powder, m.p. 196–210°. One recrystallization from acetone–petroleum ether (64–66°) gave 0.4 g. (58%), m.p. 217–220°. An aliquot (150 mg.) on further recrystallization gave 120 mg., m.p. 219.5–221°, $\lambda_{\max}^{\text{nujol}}$ 3450 cm.$^{-1}$ (11-hydroxy), 1259 cm.$^{-1}$ (weak absorption), no carbonyl absorption; $[\alpha]^{26}\mathrm{D}$ −71° (25.5 mg., chloroform, $\alpha\mathrm{D}$ −0.90°).

Anal. Calcd. for $C_{23}H_{34}O_5$ (390.50): C, 70.74; H, 8.78. Found: C, 70.98; H, 8.72.

Δ^5-Androstene-11α-ol-3,17-dione-11-acetate-3,17-di-ethylene Ketal.—The free steroid (100 mg.) in pyridine was acetylated at room temperature, and afforded 53 mg. of acetate (recrystallized from acetone–methanol), m.p. 199–200°, $\lambda_{\max}^{\text{nujol}}$ 1718 cm.$^{-1}$ (11-acetoxy), 1252 cm.$^{-1}$ (strong absorption, 11-acetoxy), no hydroxyl absorption; $[\alpha]^{25}\mathrm{D}$ −92° (12.2 mg., chloroform, $\alpha\mathrm{D}$ −0.56°).

Anal. Calcd. for $C_{25}H_{36}O_6$ (432.54): C, 69.42; H, 8.39. Found: C, 69.27; H, 8.25.

Δ^4-Androstene-11α-ol-3,17-dione.—A solution of the 11α-ol-3,17-diketal (200 mg., m.p. 217–220°) in 5 ml. of glacial acetic acid was heated on the steam-bath, and was treated with 2 ml. of water. The heating was continued for 25 minutes when additional water was added. The mixture was cooled and neutralized with sodium bicarbonate solution. The crystals were collected and washed with water, 100 mg. (60%), m.p. 224–227°. Two recrystallizations from acetone–petroleum ether (64–66°) gave 65 mg., m.p. 227.5–229°, $\lambda_{\max}^{\text{abs. alc.}}$ 241 mμ, ε 14,800; $\lambda_{\max}^{\text{nujol}}$ 3390 cm.$^{-1}$ (11-hydroxy), 1735 cm.$^{-1}$ (17-keto), 1645 cm.$^{-1}$ (3-keto), 1606 cm.$^{-1}$ (Δ^4); $[\alpha]^{25}\mathrm{D}$ +165° (11 mg., chloroform, $\alpha\mathrm{D}$ +0.91°), $[\alpha]^{25}\mathrm{D}$ +146° (11.5 mg., absolute alcohol, $\alpha\mathrm{D}$ +0.84°); literature[2]: m.p. 226–227°, $[\alpha]^{24}\mathrm{D}$ +162° (chloroform).

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(9) This preparation was carried out by Robert Lenhard.

(10) T. Reichstein, *Helv. Chim. Acta*, **20**, 953 (1937).

(11) We wish to thank William Fulmor for the infrared spectrograms.

(12) R. Antonucci, S. Bernstein, R. Littell, K. J. Sax and J. H. Williams, *J. Org. Chem.*, **17**, 1341 (1952).

(13) We wish to thank Louis M. Brancone, Samuel S. Modes and Edward B. Ruffing, Jr., for the microanalytical data.

The High Field Conductance of Aqueous Solutions of Glycine at 25°[1]

BY DANIEL BERG AND ANDREW PATTERSON, JR.

RECEIVED OCTOBER 4, 1952

The high field conductance of aqueous solutions of glycine, in the order of 0.1 to 1.6 molar, has been measured relative to hydrochloric acid at 25°. Two previous determinations of the high field conductance of glycine solutions have been reported.[2,3] These two sets of determinations are not in agreement with the observations reported herewith, and accordingly some discussion and explanation are in order. In this connection our results for a group of preliminary experiments on three separate samples of glycine are informative; these results are also presented briefly.

Experimental and Results

Both low and high field conductance measurements were carried out according to the procedure of Gledhill and Patterson[4] using a differential pulse transformer bridge circuit. The temperature control was to within 0.015°; the temperature of 25° was established with reference to a recently calibrated platinum resistance thermometer.

One conductance measurement was made on an unpurified stock sample of glycine. In this case the solid amino acid was added to the conductance cell with a spatula until a desired resistance was obtained. The concentration was determined to be approximately 0.12 molar by evaporating the water from a weighed portion of the solution and weighing the residue. The results obtained are shown as the lowest curve in Fig. 1. A second determination was made on a three-times recrystallized portion of the material originally employed. The glycine was recrystallized from conductivity water, filtered under suction, washed, and finally dried in a desiccator over sulfuric acid. The amount of material obtained was sufficient only to bring the cell resistance to approximately 3600 ohms, which was higher than desired. The concentration was approximately 0.6 molar. The results of the high field conductance determination on this solution are shown as the highest curve in Fig. 1. Because of the striking difference between these results and those obtained on the unpurified sample, approximately 10^{-5} mole of ammonium chloride was added to the liter of glycine solution in the conductance cell to bring the resistance to 1200.0 ohms and the high field conductance redetermined on the mixed electrolyte solution. The results are shown as curve C of Fig. 1. Finally, determinations were made on a once-recrystallized sample of Eastman ammonia-free glycine. The results of two determinations on the same solution are shown as curve B of Fig. 1. The concentration of the glycine solution was 1.644 molal, determined from the carefully weighed quantities of glycine and conductivity water used in preparation of the solution. In all cases a hydrochloric acid solution of appropriate resistance was used as reference solution.

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(1) Contribution No. 1101 from the Department of Chemistry Yale University.

(2) M. Wien, *Phys. Z.*, **32**, 545 (1931).

(3) O. Blüh and F. Terentiuk, *J. Chem. Phys.*, **18**, 1664 (1950).

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Discussion

No claim is made for the accuracy of curves C or D; they indicate the importance of removal of other electrolytes from the glycine solution. Curve B conforms sufficiently to a straight line to convince one that a solution of carefully purified glycine behaves as do solutions of weak electrolytes. In comparison with acetic acid the results for glycine are, at 50 kv./cm., 1.8%; for acetic acid at the same field, 1.75%; at 100 kv./cm., glycine, 3.92%; acetic acid, 4.86%. The slope of the acetic acid curve is greater and the negative intercept of the curve is greater; glycine appears accordingly somewhat stronger than acetic acid. However, the concentration of the acetic acid, the data for which are taken from Bailey and Patterson,[5] was 7.405×10^{-4} molar, while the concentration of the glycine solution was 1.644 molar. It is obviously unwarranted to compare the high field conductance of glycine and acetic acid in terms of so simple a concept as relative strongness or weakness. Glycine has been shown to be principally in the form of zwitterions in solution: $NH_3^+CH_2COO^-$. The comparatively very high concentration of glycine required to provide an appreciable electrolytic conductance is in accord with this fact. This being so, the necessity of using very carefully purified materials is apparent. The *p*H of the solution used for curve B was measured as 5.9; the isoelectric *p*H of glycine is 5.96. The acid and base ionization constants are given as[6] $K_a = 4.47 \times 10^{-3}$; $K_b = 6.04 \times 10^{-5}$ at 25°. We may therefore conclude that the ionic entities present in greater concentration and thus the equilibrium more likely to be affected by the high field are represented by the acid ionization

$$(NH_3CH_2COOH)^+ \rightleftarrows NH_3^+CH_2COO^- + H^+$$

while the basic ionization

$$(HONH_3CH_2COO)^- \rightleftarrows NH_3^+CH_2COO^- + OH^-$$

is of lesser importance. With these assumptions, it is proper to conclude that, as with acetic acid,[5] the conductance is principally due to hydrogen ion and that one is dealing with a stronger acid, $K(0) = 4.47 \times 10^{-3}$, than acetic acid, $K(0) = 1.75 \times 10^{-5}$. It is thus natural that the slope of the high field conductance curve should be smaller than that of acetic acid.

Schiele's experimental data[7] for chloroacetic acid, $K(0) = 1.38 \times 10^{-3}$ at 25°, are drawn as curve E in Fig. 1 for comparison. It is not possible to compute a theoretical curve for glycine due to lack of necessary data. The comparison with Schiele's data is only approximate because the temperature of Schiele's measurement is not known, the $K(0)$'s do not correspond exactly, and glycine has both a K_a and a K_b, but the comparison does suggest a reasonable explanation for the magnitude of Wien effect observed with glycine. The small negative intercept of the extrapolated curve B indicates that some interionic attraction effects are present.

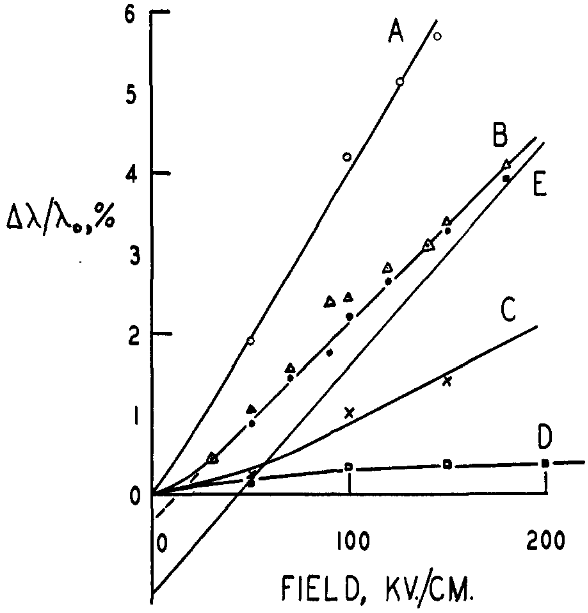

Fig. 1.—The high field conductance of aqueous solutions of glycine at 25°: A, carefully purified glycine, 0.6 molar; B, two determinations on a solution of carefully purified glycine, 1.644 molal; C, same solution as for curve A with approximately 10^{-5} mole of ammonium chloride added; D, unpurified stock sample of glycine, approximately 0.12 molar; E, Schiele's data (ref. 7) for chloroacetic acid.

It is also notable that curve A, for glycine at the smaller concentration 0.6 molar, compared to 1.6 molar for curve B, exhibits a larger Wien effect. In the more dilute solution a proportionately larger contribution might be expected from the weaker basic ionization equilibrium, so that the change of $K(X)$ with increasing field would be greater.

Our data do not agree with those of Wien[2] or of Blüh and Terentiuk.[3] Wien's results show a curve typical of a strong electrolyte and a Wien effect of about 5% at 100 kv./cm., while the concentration is reported as 5×10^{-5} molar. Since no data are given by Wien on the conductance cell constant or the source or preparation of his sample, it can only be assumed that the aminoacetic acid employed was highly contaminated by strong electrolytes. Blüh and Terentiuk report measurements at three values of field: at 60 kv./cm., 4.8%; at 80 kv./cm., 7.6 and 7.0%; and at 100 kv./cm., 10.0%; and for two concentrations, 64.0 g./l. and 38.1 g./l. (Our concentration for curve B was approximately 120 g./l.; for curve A, approximately 45 g./l.) These values of Wien effect are considerably larger than those which we report herewith.

Blüh and Terentiuk report a fractional high field conductance quotient of 4.2% for a solution containing 0.040 g. potassium chloride per liter, at 100 kv./cm. For such a solution the Onsager–Wilson equations[5] give a high field conductance quotient of 0.336% at 25°; we have found the Onsager–Wilson calculation entirely adequate to permit accurate computation of high field conductance for such a well known and simple valence type electrolyte as potassium chloride. The circuit diagram given by Blüh and Terentiuk does not appear to show any arrangement for reactance balancing, and accord-

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[5] F. E. Bailey and A. Patterson, THIS JOURNAL, **74**, 4756 (1952).

[6] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 2d ed., Reinhold Publishing Corp., New York, N. Y., 1950.

[7] J. Schiele, *Ann. Physik*, [5] **13**, 811 (1932).

ingly the results obtained for cell resistance would not reveal the true electrolytic resistance, but rather the cell impedance. If the usual parallel R–C circuit is assumed for a conductance cell, the apparent resistance equivalent of the impedance will be lower than the resistive component and the high field conductance quotients calculated from the data will be too large. Furthermore, should the capacitive component of the cell impedance change with field, additional difficulties of interpretation would result. This may be the explanation for the high values of Wien effect for potassium chloride reported in ref. 2, and for the disparity between our data and those of ref. 2 for glycine. It would require quite involved instrumentation to provide the successive pulse method of Blüh and Terentiuk with a means for reactive balancing at a 100 pulses/second repetition rate unless the rate of rise of the field were made quite slow.

We found no evidence in the series of measurements reported herewith of unusual or notable dielectric behavior of the glycine solutions with increasing field. As with the determinations on acetic acid,[5] it was found necessary to employ hydrochloric acid as reference electrolyte in order to avoid apparent bridge unbalance due to polarization occurring in different degree in the measurement and in the reference cells.

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The High Field Conductance of Lanthanum Ferricyanide at 25°[1]

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The high field conductance of lanthanum ferricyanide is of interest because the compound is a 3–3 valence-type electrolyte. Conductance data at low fields are available for it,[2] and it thus is possible to test the Onsager–Wilson theory[3] as well as the correction thereto suggested by Bailey and Patterson.[4] Previous determinations on 2–2 valence-type electrolytes have been reported for magnesium sulfate,[5] zinc sulfate[6] and copper sulfate.[7] High field conductance measurements for lanthanum ferricyanide have not been previously reported. We have determined the high field conductance of aqueous solutions of lanthanum ferricyanide, approximately 10^{-4} molar, relative to potassium chloride at 25°.

Determinations were made on three solutions of lanthanum ferricyanide of slightly differing concentration. The procedure employed was identical with that of Gledhill and Patterson.[6] All measurements were made with four microsecond pulse duration. The lanthanum ferricyanide employed was a C.P. sample from the Delta Chemical Works, New York City; it was prepared from lanthanum nitrate and potassium ferricyanide and it is thus probable that there was some potassium nitrate present as contaminant. The sample was guaranteed to be better than 99% pure; we shall discuss the probable purity of the sample in terms of the conductance results obtained with it. The lanthanum ferricyanide was used in the form of a strong stock solution, approximately 0.013 molar; the solutions for conductance determinations were prepared by weight dilution with conductivity water in the conductance cells. The potassium chloride reference solutions were of such concentration as to give a suitable resistance in the comparison cell, and thus near 3×10^{-4} molar. The temperature was maintained at $25 \pm 0.015°$ referred to a recently calibrated platinum resistance thermometer.

The results are presented in Fig. 1 as three curves, B, C and D, for solutions of concentrations 1.032×10^{-4} molar, 1.025×10^{-4} molar, and 1.023×10^{-4} molar, respectively, based upon the formula $La(Fe(CN)_6)\cdot 5H_2O$. Curve A is a portion of the data computed according to the procedure outlined in ref. 4; curve E is for the Onsager–Wilson theory.[3] It will be observed that at 200 kv./cm. the fractional high field conductance quotient has a value of some 20% compared with a value of 3.3% for magnesium sulfate and with a value of 0.41% for potassium chloride, all at equivalent concentrations. At the same field the Onsager–Wilson theory yields a value of 7.39%, and the calculation of Bailey and Patterson[4] a value of 36.3%; both values depart widely from the quantity experimentally observed, curve B. The experimental results bend over in the manner characteristic of strong electrolytes even though the fractional high field conductance quotient is quite large. Filled circles near curve B will be discussed below.

In previous work we have found that a small amount of electrolytic impurity in the presence of an electrolyte under study may profoundly alter the shape of the Wien effect curve and the magnitude of the Wien effect. Glycine was found[8] to be especially sensitive in this respect: only 10^{-5} mole of ammonium chloride in a 0.6 molar glycine solution was sufficient entirely to alter the nature of the results obtained. It is thus necessary to demonstrate the effects of possible impurities such as potassium nitrate on the high field conductance results.

If we assume that there was present in the lanthanum ferricyanide 1% of potassium nitrate, and if we further assume that the same results would obtain if the pure salts were placed in separate conductance cells rather than (as in the actual experiment) in the same conductance cell, and the two cells then operated in parallel, we may calculate as follows: For potassium nitrate the value of Λ^0 is 145 and the concentration is 10^{-6} molar; for the lanthanum ferricyanide Λ^0 is 168 and the concentration is 10^{-4} molar. The resistance of the potassium nitrate solution will thus be approximately 100 times that of the lanthanum ferricyanide. If the resistance of the lanthanum ferricyanide solution is 1010 ohms and that of the potassium nitrate 101,000 ohms, the parallel circuit will have a resistance of 1000 ohms. If the resistance of the lantha-

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[1] Contribution No. 1132 from the Department of Chemistry, Yale University.

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[3] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd ed., Reinhold Publishing Corp., New York, N. Y., 1950.

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[5] F. E. Bailey and A. Patterson, *ibid.*, **74**, 4428 (1952).

[6] J. A. Gledhill and A. Patterson, *J. Phys. Chem.*, **56**, 999 (1952).

[7] D. Berg and A. Patterson, THIS JOURNAL, **74**, 4704 (1952).

[8] D. Berg and A. Patterson, *ibid.*, submitted for publication.