$$+ \text{H}^+ \longrightarrow \qquad (1)$$

$$\longrightarrow \qquad (2)$$

$$\longrightarrow \qquad + \text{CH}_3\text{OH} + \text{H}^+ \qquad (3)$$

In reaction (2) the nucleophilic methine carbon of the diazoketone is attacked by a proton to give an aliphatic diazonium ion[6] which then loses nitrogen by a displacement reaction on carbon involving an unshared electron pair on oxygen (equation (2)).[7] The oxonium ion thus formed is then attacked by the solvent water to give coumaranone and methanol and at the same time the proton is regenerated. Reactions (2) and (3) might well be concerted. Although this scheme conforms with the catalytic nature of the action of the hydrochloric acid, the acid will be partially consumed by an alternative final step—the attack of a chloride ion on the oxonium intermediate

$$\longrightarrow \qquad + \text{CH}_3\text{Cl} \qquad (4)$$
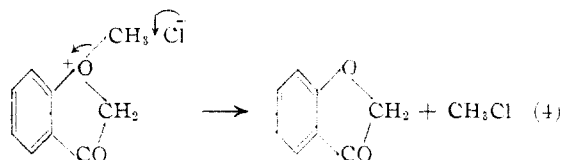
However, this will only occur as a side reaction since the presence of water in large excess ensures much more frequent attack by solvent than by chloride ion.

It is of interest in connection with the present work to consider a recent report by Seth and Deshapande[8] that α-diazo-o-methoxyacetophenone decomposes spontaneously with the evolution of nitrogen to give a crystalline solid, m.p. 104°. This substance was assigned the molecular formula $C_9H_8O_2$ and two derivatives were described but no structure assignation was made. The properties of this product (Table I) and its source suggested to us that it might be coumaranone. Our sample of α-diazo-o-methoxyacetophenone, however, gave no visible evidence of decomposition on standing at 25–28° for six days; furthermore, the intensity and position of bands in the infrared spectrum of the diazoketone before and after storage were identical in every respect, confirming that pure α-diazo-o-methoxyacetophenone does not decompose spontaneously.[9]

(6) Cf. J. F. Lane and R. L. Feller, THIS JOURNAL, **73**, 4230 (1951).

(7) The geometry of the system favors this reaction rather than direct attack on the diazonium ion by the solvent, as in the case of simple diazoketones (cf. ref. 6).

(8) U. S. Seth and S. S. Deshapande, J. Ind. Chem. Soc., **27**, 429 (1950).

(9) It is noteworthy that neither Marshall, Kuck and Elderfield[1] nor P. Pfeiffer and E. Enders, Ber., **84**, 247 (1951), report any spontaneous decomposition of their samples of this diazoketone.

Table I

	Seth and Deshapande's product	Coumaranone
Melting point, °C.	104	101–102[a]
Analysis:	$C_9H_8O_2$ requires:	$C_8H_6O_2$ requires:
Found:		
C, 72.5; H, 4.7	C, 73.0; H, 5.4	C, 71.6; H, 4.5
Molecular weight:		
Found: 140	148	134
Semicarbazone:		
Melting point, °C.	220	231[b]
Analysis:	$C_{10}H_{11}O_2N_3$ requires	$C_9H_9O_2N_3$ requires
Found: N, 21.2	N, 20.5	N, 22.0
Product with bromine:		
Melting point, °C.	147	142[c]
Analysis:	$C_9H_8O_2Br_2$ requires	$C_8H_4O_2Br_2$ requires
Found: Br, 53.1	Br. 52.0	Br, 54.8

[a] D. A. Clibbens and M. Nierenstein, J. Chem. Soc., 1493 (1915). [b] R. Stoermer and F. Bartsch, Ber., **33**, 3178 (1900). [c] K. Fries and W. L. Pfaffendorf, ibid., **45**, 161 (1912).

Experimental

α-Diazo-o-methoxyacetophenone.—An ethereal solution of 3 g. of o-methoxybenzoyl chloride[10] was added drop by drop with thorough shaking to an ethereal solution of a large excess (about 4 molar equivalents) of diazomethane at 0°. After a brief induction period nitrogen was evolved vigorously. The reaction mixture was allowed to stand overnight at room temperature and was then filtered to remove a small amount of solid that had separated. After removing the excess diazomethane and ether by distillation under reduced pressure at 30–40° a golden yellow oil (3.1 g., quantitative yield) was obtained. A sample on standing at room temperature (25–28°) for six days showed no visible sign of decomposition and its infrared spectrum was found to be identical with that of the freshly prepared material.

Coumaranone.—In a flask fitted with a calibrated dropping funnel and connected to a gas buret were placed 1 g. of α-diazo-o-methoxyacetophenone and 5 ml. of distilled water. To this was added by means of the dropping funnel, 0.1 ml. of 1.13 N hydrochloric acid during vigorous stirring with a magnetic stirrer; a steady evolution of gas was observed. A second 0.1 ml. of acid was added after 1 hour, when the gas evolution had slackened. The reaction was complete in three hours with the evolution of one molar equivalent of nitrogen. Further addition of acid was without effect. The crystalline solid that had separated was collected by filtration and dried. A light yellow solid (0.65 g., 86.5%), m.p. 95–97°, was thus obtained. Purification by sublimation at 1 mm. gave an almost colorless crystalline powder of m.p. 100–101.5°, undepressed on admixture with an authentic sample of coumaranone.

(10) J. T. Marsh and H. Stephen, J. Chem. Soc., 1635 (1925).

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The High Field Conductance of Copper Sulfate Relative to Potassium Chloride at 25°[1]

BY DANIEL BERG AND ANDREW PATTERSON, JR.

The high field conductance of magnesium sulfate has been determined by Bailey and Patterson.[2] It was found that the high field conductance was insensitive to change of temperature over the range 5–55° when plotted as the fractional high field conductance quotient, $\Delta\lambda/\lambda_0(\%)$, although the actual conductance varied markedly with temperature. It was also found that the experimental results were decidedly larger than the values pre-

(1) Contribution No. 1100 from the Department of Chemistry, Yale University.

(2) F. E. Bailey and A. Patterson, THIS JOURNAL, **74**, 4426 (1952).

dicted by the Onsager–Wilson theory[3]: the difference at 200 kv./cm. between the theoretical and experimental results was 1.5. A similar determination of high field conductance of a zinc sulfate solution showed a larger change of conductance with increasing field and the same type of disparity between the theoretical and experimental results: the difference at 200 kv./cm. was 1.7.[4] Bailey and Patterson[5] found it possible to make a correction for the "weakness" of the two 2–2 electrolytes on the assumption that ion pairs were present which had a calculable Wien effect characteristic of a weak electrolyte. The agreement between the corrected theory and the experimental results was gratifying.

In order to check the high field conductance of another 2–2 electrolyte and the success of the corrected theory[5] in the computation of the Wien effect for such an electrolyte, copper sulfate was chosen since the low field conductance data, required for the correction, were available for it.[3] The measurement was made at 25° only since in view of the results with magnesium sulfate[2] it was deemed unnecessary to study other temperatures.

Determinations of high field conductance were made on two different copper sulfate solutions, having very nearly the same concentration, approximately 1.77×10^{-4} molar. The concentration of the potassium chloride reference solution was 3.18×10^{-4} molar. Both salts were purified by repeated crystallizations from conductivity water and made up in strong stock solutions in conductivity water. The solutions for actual conductance measurement were made by weight dilution of the strong solutions to give suitable resistance values in the conductance cells: R_0 ($CuSO_4$) = 1026.0 ohms; R_0 (KCl) = 921.5 ohms. The concentration of the potassium chloride stock solution was determined from the weight of fused potassium chloride and water used; the concentration of the copper sulfate stock solution was obtained from low field conductance measurements. The determination of high field conductance was done in exactly the same manner as described by Gledhill and Patterson.[4] The results are given in Fig. 1.

Figure 1 shows the computed Onsager–Wilson theory relative to potassium chloride, uncorrected, on the lowest curve and the corrected Onsager theory on the highest curve. The experimental results for copper sulfate are shown as open and filled circles for the two separate determinations. The increase in conductance with field is greater for zinc sulfate than for magnesium sulfate, and greater for copper sulfate than for zinc sulfate, as would be expected from the successively decreasing values of $K(O)$ for the three electrolytes. It will be observed that the agreement between theory and experiment is greatly improved by the correction for the weakness of the electrolyte. The computation was made with values for $K(O)$ =

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

(4) J. A. Gledhill and A. Patterson, J. Phys. Chem., scheduled for publication, December, 1952.

(5) F. E. Bailey and A. Patterson, This Journal, 74, 4428 (1952).

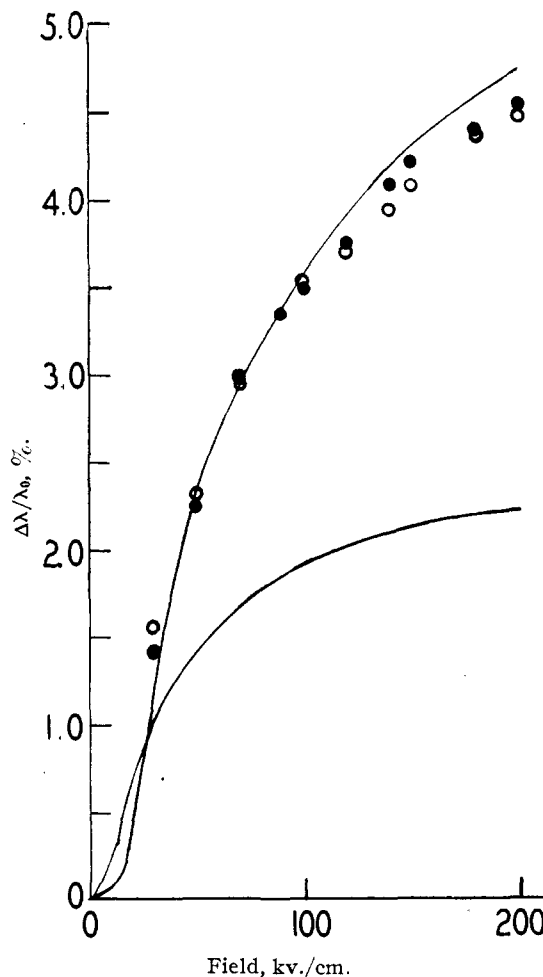Fig. 1.—The high field conductance of copper sulfate (1.77×10^{-4} molar) relative to potassium chloride at 25°; highest curve, corrected Onsager–Wilson theory; lowest curve, uncorrected Onsager–Wilson theory; closed and open circles, experimental results on two separate solutions of very nearly same concentration.

0.0043 and Λ^0 = 133.6 for copper sulfate[3]; the value 0.88 was used for $\gamma_{\pm}$ at zero field, obtained from a plot of data from Harned and Owen.[3] Whereas the disparity between the values of $\Delta\lambda/\lambda_0$ (%) at 200 kv./cm. for the experimental results and the uncorrected theory is 2.25, the theory being the lower, this difference is reduced to 0.25 in the case of the corrected theory, the theory being higher. It was found[5] that the corrected theory for both magnesium sulfate and zinc sulfate lay above experiment, a fact attributed to uncertainty in the value of $K(O)$. The agreement in the case of copper sulfate is better than for either magnesium or zinc sulfate; this is probably more or less accidental, depending upon the value of $K(O)$ chosen as a result of extrapolation of low field conductance data. There is no obvious physical interpretation to be placed on the fact that all three salts show the same effect, with the corrected theoretical curves falling slightly above the experimental.

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