heated ten hours at 210-230°. There was no perceptible reaction. The mixture was refluxed twenty minutes at 280°, at which temperature it completely resinified.

These amidines were tested on ducks and proved to be extremely toxic.

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RECEIVED NOVEMBER 5, 1948

The Oxidation of Certain Ketones to Acids by Alkaline Hypochlorite Solution

BY MARTIN W. FARRAR AND ROBERT LEVINE

The advantages of hypohalite oxidation of methyl ketones[1,2] are well recognized, yet apparently little is known of the behavior of higher alkyl ketones under similar conditions.[3] We have found that higher alkylaryl and alkylheterocyclic ketones may likewise be cleaved in good yields to carboxylic acids by hypohalite oxidation. A detailed study on the stoichiometry and mechanism of this reaction is now in progress in this Laboratory.

Procedure.—A solution of sodium hypochlorite is prepared from 50 g. of "HTH" following the directions in the literature.[1] The solution is heated to 55°, and 0.1 mole of the ketone to be oxidized is added dropwise to the rapidly stirred solution, keeping the temperature at 60-70°. After the addition of the ketone is completed (about fifteen minutes), the reaction mixture is stirred at 70° for thirty minutes. Any unreacted sodium hypochlorite is then destroyed with sodium bisulfite solution. The contents of the flask is then heated to 100°, stirred and heated for fifteen minutes longer and then cooled to room temperature. The reaction mixture is then extracted with ether to remove any unreacted ketone, and the phases separated. The aqueous phase is acidified with concentrated hydrochloric acid. The crude acid is filtered on a Büchner funnel and recrystallized from hot water. In this way the following acids were obtained: benzoic, m. p. 121-122°[4] (64%) from propiophenone, 2-thiophenic, m. p. 129-130°[5] from *n*-propyl 2-thienyl ketone, and 5-methyl-2-thiophenic, m. p. 137-138°[6] (67%) from 5-methyl-2-propionylthiophene.

In the preparation of 2-furoic acid (59%) from ethyl 2-furyl ketone the procedure followed is similar to that described above except that the temperature of the reaction mixture is never allowed to rise above 65° during the addition of the ketone and the reaction is then completed by stirring the contents of the flask at 65° for fifteen minutes after the addition of the ketone is completed. The reaction mixture is then acidified, extracted with ether, and the solvent distilled. The residue solidified. Recrystallization of this solid gave 2-furoic acid, m. p. 131-132°[6] (59%).

CONTRIBUTION No. 707
DEPARTMENT OF CHEMISTRY
UNIVERSITY OF PITTSBURGH
PITTSBURGH, PENNSYLVANIA
RECEIVED JANUARY 21, 1949

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[1] Newman and Holmes, "Organic Syntheses," 2nd Coll. Vol., John Wiley and Sons, Inc., New York, N. Y., 1943, p. 428.

[2] Fuson and Bull, *Chem. Revs.*, **15**, 275 (1934).

[3] Although Schmidt (*Arch. Pharm.*, **252**, 96 (1914)) reported that the interaction of propiophenone with alkaline hypoiodite solution gives iodoform as one of the oxidation products, he did not report the isolation of any other compounds. In repeating his work, we have isolated benzoic acid as well as iodoform.

[4] Riessert, *Ber.*, **23**, 2244 (1890).

[5] Hartough and Conley, THIS JOURNAL, **69**, 3097 (1947).

[6] Heinzelmann, *Ann.*, **193**, 192 (1878).

Extrapolation of Conductance Data for Weak Electrolytes

BY RAYMOND M. FUOSS AND THEODORE SHEDLOVSKY

Unambiguous extrapolations of conductance data, in order to determine Λ_0, the limiting conductance, and K, the dissociation constant for weak electrolytes, are possible in aqueous systems by synthesizing a hypothetical conductance curve for the completely dissociated portion of the weak electrolyte from conductance data on the corresponding strong electrolytes,[1] *e.g.*

$$\Lambda^*_{(\mathrm{HAc})} = \Lambda_{(\mathrm{HCl})} - \Lambda_{(\mathrm{NaCl})} + \Lambda_{(\mathrm{NaAc})} \qquad (1)$$

in which the Λ values refer, of course, to the same ion concentration. The degree of dissociation is then given by Λ/Λ^*, since $\Lambda = 1000\kappa/c$ and $\Lambda^* = 1000\kappa/c_i$, κ being the specific conductance, c the equivalent electrolyte concentration, and c_i the corresponding free ion concentration.

In non-aqueous systems, where the dielectric constant of the solvent is about 40 or less, this procedure cannot be employed since no strong electrolytes exist in such solvents. It therefore becomes necessary to evaluate Λ_0 and K from the conductance data for the electrolyte itself. Two extrapolation methods have been proposed.

Fuoss and Kraus[2] wrote for 1–1 electrolytes

$$\Lambda = \gamma\,(\Lambda_0 - \alpha\sqrt{c\gamma}) \qquad (2)$$

where γ is the degree of dissociation defined as the ratio of the concentration of free ions to the stoichiometric concentration c and α is the Onsager coefficient

$$\alpha = 8.2 \times 10^5\Lambda_0/(DT)^{3/2} + 82/\eta(DT)^{1/2} \qquad (3)$$

where D is the dielectric constant, η the viscosity of the solvent, and T the absolute temperature. Equation (2) was solved for γ in terms of a function[3] $F(z)$ where

$$z = \alpha\sqrt{c\Lambda}/\Lambda_0^{3/2} \qquad (4)$$

and

$$\gamma = \Lambda/\Lambda_0\, F(z) \qquad (5)$$

Substituting Eq. (5) in the mass action equation and rearranging, one obtains

$$F/\Lambda = 1/\Lambda_0 + c\Lambda f^2/FK_F\Lambda_0^2 \qquad (6)$$

where f is the activity coefficient which is computed from $(-\log f) = \beta\sqrt{c_i}$. A plot of F/Λ against $c\Lambda f^2/F$ is linear at low concentrations and extrapolates to the reciprocal of the limiting equivalent conductance, with slope $1/K_F\Lambda_0^2$.

Shedlovsky[4] later proposed the equation

$$\Lambda = \Theta\Lambda_0 - \alpha(\Lambda/\Lambda_0)\sqrt{c\Theta} \qquad (7)$$

where Θ is the degree of dissociation. Equation (7) is a quadratic in $\Theta^{1/2}$ and is therefore much simpler to solve than Eq. (2), which is a cubic in

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[1] D. A. MacInnes, THIS JOURNAL, **48**, 2068 (1926); M. S. Sherrill and A. A. Noyes, *ibid.*, **48**, 1861 (1926); D. A. MacInnes and T. Shedlovsky, *ibid.*, **54**, 1430 (1932).

[2] R. M. Fuoss and C. A. Kraus, *ibid.*, **55**, 476 (1933).

[3] R. M. Fuoss, *ibid.*, **57**, 488 (1935).

[4] T. Shedlovsky, *Jour. Franklin Inst.*, **225**, 739 (1938).

$\gamma^{1/2}$. The solution of (7) may then be written as

$$\Theta = S(z)\Lambda/\Lambda_0 \qquad (8)$$

where $S(z) \equiv (z/2 + \sqrt{1 + (z/2)^2})^2$, and z is defined by Eq. (4). Substituting in the mass action equation and rearranging, we obtain

$$1/\Lambda S = 1/\Lambda_0 + c\Lambda S f^2/K_S\Lambda_0^2 \qquad (9)$$

Here, at low concentrations, $1/\Lambda S$ is linear in $c\Lambda S f^2$, with intercept $1/\Lambda_0$ and slope $1/K_S\Lambda_0^2$. The intercepts of Eqs. (6) and (9) are found to be identical, but the slopes, and therefore the dissociation constants[5] are sometimes different. The question naturally arises as to which of the two values to choose for the dissociation constant in such cases.

The derivation[2] of Eq. (2) is based on the Onsager limiting law

$$\Lambda = \Lambda_0 - \alpha\sqrt{c} \qquad (10)$$

If Onsager had computed resistance instead of conductance, the limiting law would have read

$$1/\Lambda = 1/\Lambda_0 + (\alpha/\Lambda_0^2)\sqrt{c} \qquad (11)$$

which rearranges to

$$\Lambda = \Lambda_0 - \alpha(\Lambda/\Lambda_0)\sqrt{c} \qquad (12)$$

Shedlovsky[4] has shown that Eq. (12) reproduces conductance data to significantly higher concentrations than does Eq. (10). The derivation[4] of Eq. (7) was based on the Onsager limiting law in the form (12), and results based on Eq. (9) are therefore to be preferred.

The difference between the various functions is illustrated in Fig. 1. Curve 2 represents actual data for potassium chloride[6] where $\Lambda_0 = 149.9$ and $\alpha = 93.9$. Curve 4 is for the familiar Onsager linear limiting Eq. (10). Curve 3 is for Eq. (12), using the same constants; it will be noted that it gives a closer approximation of the experimental results than Curve 4, *i.e.*, Eq. (10). Data for iodic acid,[7] a somewhat weak electrolyte, for which $K = 0.16$, $\Lambda_0 = 391.2$, $\alpha = 150$ are plotted in Curve 5. Although, strictly speaking, the abscissa, $\sqrt{c_i}$, depends on how c_i is computed, *e.g.*, by the Fuoss or by the Shedlovsky function, these differences are too small to appear in Curve 5 on the scale of the figure. Due to ion association[8] (weak electrolytes) there are found strong negative deviations from the Onsager conductance equation, such as in Curve 5. The curves 2, 3 and 4 for potassium chloride are for $\Lambda/\Lambda_0 = (1000\kappa/c)(1/\Lambda_0)$ *vs.* $\sqrt{c_i}$, but since this salt is a strong electrolyte $c_i = c$. The slope of the linear Curve 4, $(\alpha/\Lambda_0)_{KCl}$ is 0.63, whereas the corresponding value for the ionized portion of iodic acid, $(\alpha/\Lambda_0)_{HIO_3}$ is 0.38. Let us change the ordinate scale for these three curves so that the slope for Curve 4 is 0.38 instead of 0.63. We may then suppose that the curves 2, 3 and 4 refer to $(1000\kappa/c_i)(1/\Lambda_0)$ *vs.* $\sqrt{c_i}$ for iodic acid instead of potassium chloride, and recall that for a weak electrolyte c_i is the product of the stoichiometric concentration and of the degree of dissociation. The latter is therefore obtained as the ratio of $\Lambda/\Lambda_0 = (1000\kappa/c)(1/\Lambda_0)$ to $(1000\kappa/c_i)1\Lambda_0$ at the same value of $\sqrt{c_i}$. Thus, the Fuoss function assumes that cb/db is a measure of the degree of dissociation, while the Shedlovsky function uses the ratio cb/ab, which is a better approximation, and incidentally the one which would naturally have been used if the limiting Onsager equation had been originally presented in the form of Eq. (11). The synthetic method (Eq. (1)) uses the ratio cb/fb but as we have already pointed out, it is not available in solvents with dielectric constants below 40.

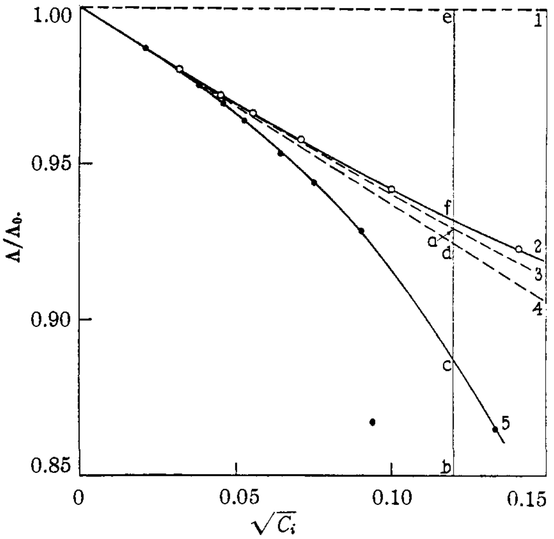

Fig. 1.—Comparsion of Conductance Functions.

Extrapolation by Eqs. (6) or (9) is essentially use of the Ostwald dilution law, corrected for the effect of long range interionic forces on mobility and thermodynamic potential; the degree of dissociation in the classical theory, Λ/Λ_0, is measured by the ratio cb/eb of Fig. 1.

The difference between K_S and K_F can be found as follows. By equating the two expressions, Eqs. (2) and (7) for Λ, substituting Eqs. (5) and (8) and solving, we obtain

$$\gamma = \Theta[1 + z(F^{-3/2}S^{-1} - S^{-1/2})] \qquad (13)$$

$$\equiv \Theta(1 + x) \qquad (13')$$

If we now substitute (13) in the mass action Eq. (6) and rearrange, we obtain

$$1/\Lambda S = 1/\Lambda_0 + c\Lambda S f^2(1 + x)^2/K_F\Lambda_0^2 + x/\Lambda_0 \qquad (14)$$

Expansion of $S(z)$ and $F(z)$ in their power series gives

$$x = z^2 + O(c^{3/2}) \qquad (15)$$

and at low concentrations Eq. (14) thus reduces to

$$1/\Lambda S = 1/\Lambda_0 + c\Lambda S f^2/K_F\Lambda_0^2 + \alpha^2 c\Lambda/\Lambda_0^4 \qquad (16)$$

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[5] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 1943; p. 190.

[6] T. Shedlovsky, THIS JOURNAL, **54**, 1411 (1932).

[7] C. A. Kraus and H. C. Parker, *ibid.*, **54**, 2429 (1932).

[8] R. M. Fuoss, *Chem. Revs.*, **17**, 27 (1935).

The limiting slope of Eq. (16) is

$$\frac{\mathrm{d}(1/\Lambda S)}{\mathrm{d}(c\Lambda Sf^2)_{c=0}} = \frac{1}{K_F\Lambda_0{}^2} + \frac{\alpha^2}{\Lambda_0{}^4} = \frac{1}{K_S\Lambda_0{}^2} \qquad (17)$$

whence

$$1/K_S = 1/K_F + \alpha^2/\Lambda_0{}^2 \qquad (18)$$

The difference shown in Eq. (18) is a consequence of the *difference* between Θ and γ; in the limit of zero concentration, both Θ and γ approach unity, but as is readily seen from Eqs. (13′) and (15), their difference is linear in concentration, and the mass action extrapolation is essentially one on a linear concentration scale. According to Eq. (3), the ratio α/Λ_0 has the following upper bounds if we set the Walden product $\Lambda_0\eta = 0.5$: $D = 40$, $\alpha/\Lambda_0 \leqslant 2$; $D = 20$, $\alpha/\Lambda_0 \leqslant 4$; $D = 10$, $\alpha/\Lambda_0 \leqslant 8$. Since K decreases[9] rapidly as D decreases, the two methods of extrapolation will not differ significantly when K is less than about 10^{-3}. In the approximate range $10^{-3} \leqslant K \leqslant 1$, however, we recommend extrapolation by means of Eq. (9).

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(9) R. M. Fuoss and C. A. Kraus, This Journal, **55**, 1019 (1933).

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The Structure of Khellin

BY T. A. GEISSMAN

Khellin has been resynthesized by Späth and Gruber from its cleavage product, khellinone, by the application of the Kostanecki–Robinson method.[1] Since this synthesis is not entirely unamibiguous, often giving rise to mixtures of the desired chromone and the isomeric 4-methylcoumarin; and since khellin-like model compounds are not unequivocally distinguishable from the corresponding 4-methylcoumarins by absorption spectra, as recent work in this Laboratory has shown, some doubt has remained that khellin actually possesses the 2-methylchromone structure.

Khellin has now been resynthesized from khellinone by two methods which are known to lead unambiguously to 2-methylchromones, and with yields which surpass those usually recorded for the Kostanecki–Robinson reaction. Using a method analogous to that of Wittig,[2] khellinone, treated with sodium hydride in ethyl acetate, yielded a compound (A, see experimental below) which when treated with cold, concentrated hydrochloric acid was converted nearly quantitatively into khellin. The identity of the product was shown by its melting point and mixed melting point with authentic khellin (152–153°), and by analysis.

In a second experiment, khellinone acetate, treated with sodium hydride in ethyl acetate, gave the compound A. This is C-acetylkhellinone, and is converted into khellin by cold, concentrated hydrochloric acid in substantially quantitative yield.

The acylation of substituted *o*-hydroxyacetophenones to yield diketones and, ultimately, chromones is a well-known reaction. 4-Methylcoumarins have not been observed as products of these reactions.

One prior example of the conversion of an *o*-acetoxyacetophenone into the corresponding *o*-hydroxyacetylacetophenone under conditions similar to those used in this work has been recorded.[3] The analogous reaction with *o*-benzoyloxyacetophenones, leading eventually to flavone derivatives, has been used extensively. Model experiments on a number of substituted *o*-acetoxyacetophenones have shown that this procedure is general as a method for the synthesis of 2-methylchromones in good yields.

Details of these reactions and products will be reported in a later publication.

Experimental

Khellinone was prepared in 90% yield by the hydrolysis of khellin in 1% aqueous potassium hydroxide, according to the method of Späth and Gruber.[1]

C-Acetylkhellinone.—(A) To 0.5 g. of khellinone acetate in 5 ml. of dry ethyl acetate was added 0.5 g. of sodium hydride. The solution was warmed gently from time to time for an hour and allowed to stand overnight at room temperature. Crushed ice was added, followed by dilute hydrochloric acid, and the yellow solid collected by filtration. It weighed 400 mg. After recrystallization from aqueous methanol it formed pale yellow needles, which melted at about 90° when plunged into a preheated bath, but at temperatures up to about 122° when heated slowly. It is probable that this behavior is due to a slow dehydration under the influence of heat with the formation of khellin.

Anal. Calcd. for $C_{14}H_{14}O_6$: C, 60.48; H, 5.08. Found: C, 60.34; H, 5.11.

(B) To 0.5 g. of khellinone in 5 ml. of ethyl acetate was added 0.5 g. of sodium hydride. The mixture was allowed to stand overnight and worked up as in (A). The product weighed 413 mg. after recrystallization from dilute methanol.

C-Acetylkhellinone, in dilute aqueous methanol, gives with ferric chloride a momentary flash of green, the color then changing through green-brown to reddish-brown. Khellinone, under identical conditions, gives an intense, pure green.

Khellin.—To 200 mg. of C-acetylkhellinone was added 2 ml. of concentrated hydrochloric acid. The compound dissolved to give a deep orange solution. After solution was complete (about one minute) 20 ml. of water was added. Pure white needles of khellin separated (175 mg.; 94%). After recrystallization from dilute methanol it melted at 152–153° (unchanged by admixture with authentic khellin).

Anal. Calcd. for $C_{14}H_{12}O_5$: C, 64.59; H, 4.65. Found: C, 64.48; H, 4.89.

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LOS ANGELES 24, CALIF. RECEIVED JANUARY 24, 1949

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(1) Späth and Gruber, *Ber.*, **71B**, 106 (1938).

(2) Wittig, *Ann.*, **446**, 155 (1925).

(3) Virkar and Wheeler, *J. Chem. Soc.*, 1679 (1939).