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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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%).

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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).