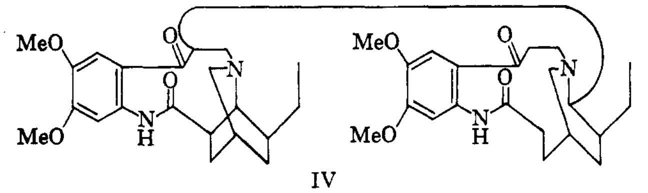
In the infrared spectrum gabonine had a set of peaks in Nujol at 1595, 1620, and 1672 cm.$^{-1}$ (broad) in good agreement with the model (1595, 1610, 1650, and 1680 cm.$^{-1}$).

An attempt was made to prove the validity of these conclusions by ring closure to a 4-quinolinol (*cf.* ring closure of the analogous yohimbine derivative[11]); the compound remained unchanged as also did the related ozonolysis product of voacangine.[12] A Dreiding model of the tetracyclic system (left-hand monomeric unit of IV) derived from ibogaline showed that the preferred configuration of the ten-membered ring was not favorable for ring closure (*cf.* an analogous situation for vobasine[13]). It may well be that the formation of iboquine by autooxidation of ibogaine does not proceed *via* a ring-opened intermediate.

When the mass spectrum of gabonine was run the molecular ion was found to be exactly twice what was expected, *viz.*, 2 × 372; hence, it is at least a dimer. The paucity of gabonine and the rareness of ibogaline makes the attempted preparation of the former from the latter impossible for the moment, and structure IV for gabonine is put forward as a working hypothesis only.



IV

In view of the known ease of autoöxidation of the iboga-class indoles,[2,3] the possibility exists that kinsantine and gabonine may be artefacts isolated instead of ibogaline, which we never detected.

[11] B. Witkop and S. Goodwin, *J. Am. Chem. Soc.*, **75**, 3371 (1953).

[12] F. Walls, O. Collera, and A. Sandoval, *Tetrahedron*, **2**, 173 (1958).

[13] M. P. Cava, S. K. Talapatra, J. A. Weisbach, B. Douglas, and G. O. Dudek, *Tetrahedron Letters*, 53 (1963).

A Study of Anodic Acetoxylation Potentials[1]

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The Kolbe electrochemical reaction is usually considered[2,3,4a] to proceed according to the free-radical mechanism that is shown in the equation following,

$$2RCOO^- - 2e \longrightarrow 2RCOO\cdot \longrightarrow 2CO_2 + 2R \longrightarrow R_2 \quad (1)$$

though attempts to make use of the Kolbe reaction for alkylation have not been particularly successful. Trinitrotoluene has been methylated to trinitroxylene[5] and pyridine alkylated to isomeric methylpyridines[6] and phenylpyridines,[7,8] all, however, in low yield. Several acyloxylations have also been reported, the acetoxylation of anisole,[9] furan,[9] and naphthalene.[10] These acyloxylations have been considered[2,3,9] to occur by attack of the acetoxy radical upon the substrate before decarboxylation could occur.

Our studies indicate, however, that, at least in the case of the formation of naphthyl acetate, the reaction probably does not proceed *via* the formation of an acetoxy radical which then adds to the naphthalene. Instead, the naphthalene molecule is first oxidized to a radical carbonium ion which then reacts further, according to the following scheme.

$$C_{10}H_8 - e \longrightarrow C_{10}H_8^+ \longrightarrow \text{products} \quad (2)$$

Experimental

We first repeated the work of Linstead, *et al.*[10] They reported a 24% yield of α-naphthyl acetate, which, however, they did not isolate. They hydrolyzed and acidified the crude product and recovered the naphthol from the steam distillate. We looked for but were not able to detect any methylnaphthalenes in either the crude reaction mixture or the steam distillate, by column chromatography. We noted no anodic gas evolution, even at current densities up to 1 amp./cm.^{2}. Since the acetoxy radical is highly unstable[11,4b] either these radicals were not formed or they reacted before they could decompose. The half-life of the acetoxy radical is estimated[11] to be of the order of 10^{-9}–10^{-10} seconds and even if the electric field exerted a stabilizing influence, it is difficult to see how the naphthalene could react with all of the radicals before they could decompose.

We then investigated the electrochemical behavior of the naphthalene–acetic acid system and other related hydrocarbon–acetic acid systems. No attempt was made to isolate and determine the reaction products, which could not have been present in more than milligram quantities. No solution was electrolyzed long enough to consume more than about 0.1% of the organic reductant.

Current density–anode potential measurements were made in solutions of potassium acetate, ammonium acetate, and zinc chloride, in anhydrous acetic acid, with and without added benzene, anthracene, and naphthalene. Anode potentials were measured using an interrupter technique to eliminate ohmic drop. The current was interrupted with an electronic circuit for 20-μsec. intervals every millisecond and the potential was determined from the voltage–time trace on a calibrated oscilloscope. The current was measured from the potential fall across a resistor in series with the circuit.

The cathode was a silver plate coated with silver chloride to avoid the evolution of hydrogen. The anode was a 1.2-cm.^{2} piece of bright platinum. (Later results using platinized titanium agreed with those on platinum.) The reference electrode was a silver–silver chloride wire. All solutions were saturated with respect to KCl or $ZnCl_2$.

The cell was a 5 × 30 cm. Pyrex glass tube into which ground glass joints were sealed to admit the solution and to hold the three electrodes. The electrodes were sealed into the glass. The joints were fitted with Teflon sleeves to avoid the use of greases but were not completely airtight. However, the deliberate addition of enough water to a previously anhydrous solution to make it about 0.25 *M* with respect to water increased the potentials at

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[1] Work was performed at the City College of the City University of New York.

[2] B. C. L. Weedon, "Advances in Organic Chemistry," Vol. 1, Interscience Publishers, Inc., New York, N. Y., 1960, pp. 1–34.

[3] E. S. Gould, "Mechanism and Structure," Holt, Rinehart, and Winston, New York, N. Y., 1959, p. 689.

[4] C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957: (a) pp. 580–582; (b) pp. 491–493.

[5] L. F. Fieser, R. C. Clapp, and W. H. Daudt, *J. Am. Chem. Soc.*, **64**, 2052 (1942).

[6] S. Goldschmidt and M. Minsinger, *Chem. Ber.*, **87**, 956 (1954).

[7] F. Fichter and H. Stenzl, *Helv. Chim. Acta*, **22**, 974 (1939).

[8] P. J. Bunyan and D. H. Hey, *J. Chem. Soc.*, 3787 (1960).

[9] C. L. Wilson and W. T. Lippincott, *J. Electrochem. Soc.*, **103**, 672 (1956).

[10] R. P. Linstead, J. C. Lunt, B. C. L. Weedon, and B. R. Shephard, *J. Chem. Soc.*, 3624 (1952).

[11] W. Braun, L. Rajkenbuch, and F. R. Eirich, *J. Phys. Chem.*, **66**, 1591 (1962).

low current density by only about 5 mv. and had no noticeable effect at high current densities. Since the effects of the organic solutes were at least an order of magnitude greater, the small amounts of moisture diffusing in through the joints or admitted during addition of the solute would be negligible. Nevertheless, as far as practicable, moisture was excluded and the reagents were dried.

The acetic acid was refluxed overnight with acetic anhydride and distilled directly into the cell, as required. The salts used were $ZnCl_2$ and mixtures of KCl with either potassium or ammonium acetate. The salts were Baker's analyzed grade, used directly with no purification other than drying. They were dehydrated by heating *in situ* at 150–190° at 10 mm. for at least 0.5 hr. Benzene (C.P.) was used without further purification. Anthracene (C.P.) was sublimed before use. The naphthalene was U.S.P. grade, sometimes used without further purification, sometimes sublimed, and sometimes column chromatographed. The purification had no apparent effect on the results of the naphthalene runs.

Current–voltage measurements were made with each salt–acid solution until reproducible results were obtained. The cell was then opened and a sample of the organic reductant was quickly added. Moisture admitted during the addition of reductant is estimated, from the humidity of the air and the cell dimensions, to be, at most, 10^{-6} moles.

The first few measurements made in each solution were usually irreproducible and with low results. However, on continuous passage of current, potentials rose and the results became reproducible. The higher the current, the shorter the time required for the potential to rise to reproducible values. This effect probably results from a clean up, either of the solution or of the electrode surface. (Pre-electrolysis with an auxiliary electrode was not practical because organic electrolysis products would have been formed.) The time taken for the current and voltage to reach steady-state values varied from solution to solution and depended on current density. Most measurements took between 5 and 20 min. per point. During that time interval, the current fell slightly and the potential rose. The curves were reproducible to ±25 mv. at higher current densities, or better than 2%.

Results and Discussion

Figure 1 shows some typical voltage–log current density curves for solutions of saturated ammonium acetate (B) and saturated potassium acetate (A). (Overvoltages could not be calculated since there were no data for the computation of the hypothetical acetate ion–acetate radical and naphthalene–naphthalene ion electrodes.) The results are in good agreement, allowing for the higher acetate ion concentration in the ammonium acetate solutions. The close correspondence of the upper plateaus is to some extent coincidental, since reproducibility from solution to solution is not that good. Nevertheless, it seems probable that the lower plateau corresponds to the oxidation of the acetate ion and the upper plateau corresponds to the oxidation of the molecular acetic acid. (There is some oxidation of the platinum, as reported by Conway.[12] Small amounts of acid-resistant material were deposited at the anode during the electrolysis.) The shapes of the curves, including the characteristic hysteresis loops are in agreement with the results reported by Conway[12] for solutions of anhydrous formic acid–potassium formate and trifluoroacetic acid–potassium trifluoroacetate.

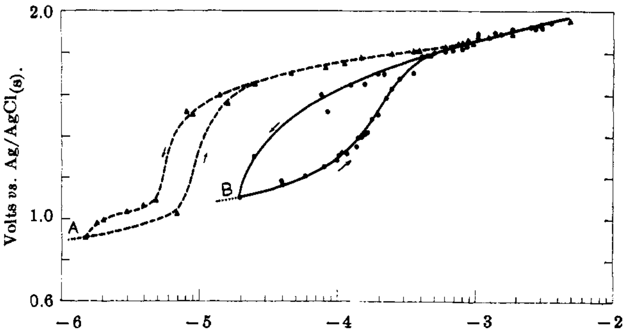

Figure 1.

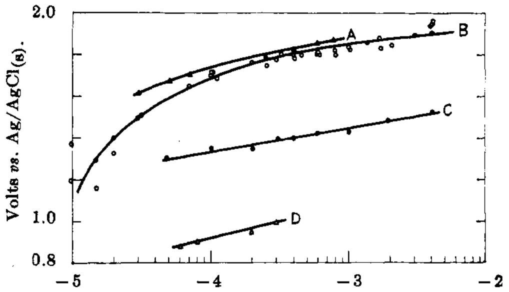

Figure 2.

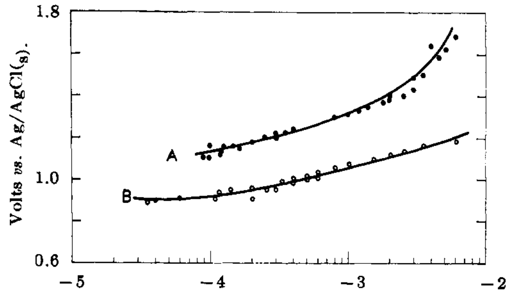

Figure 3.

Figure 2 compares a typical voltage–log current density curve for acetic acid–potassium acetate (B) with the results obtained on addition of benzene (A) or naphthalene (C) or anthracene (D) to the solution. It may be noted that the addition of benzene raised the potential somewhat while the addition of naphthalene or anthracene lowered the potential sharply. The words "lowered the potential" can be taken literally because several times the organic reductant was added while the current was running under steady-state conditions and within seconds the potential dropped by 0.4–0.8 v. The order of ease of oxidation is the same as that reported by Lund[13] and by Pysh and Yang[14] and the 0.4-g. difference observed between the oxidation potentials of anthracene and naphthalene agrees very well with the 0.47-[13] and the 0.45-v.[14] differences obtained in a different system using a different technique (*i.e.*, vibrating and rotating microelectrodes in acetonitrile *vs.* stationary steady-state macroelectrodes in acetic acid.) Results observed but not graphed indicate that curve C, for naphthalene, crosses curve B at low-current densities, in the 10^{-6}-amp./cm.^{2} range, indicating that naphthalene requires a higher oxidation potential than acetate ion but that naphthalene is probably more strongly adsorbed and displaces acetate ion from the surface.

Figure 3 shows the results obtained with $ZnCl_2$ in acetic acid, with (curve B) and without (curve A) added

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(12) B. Conway and M. Dzieciuch, *Proc. Chem. Soc.*, 121 (1962).

(13) H. Lund, *Acta Chem. Scand.*, **11**, 1323 (1957).

(14) E. S. Pysh and N. C. Yang, *J. Am. Chem. Soc.*, **85**, 2124 (1963).

naphthalene. Again, the naphthalene lowered the oxidation potential sharply. The results of Figure 3 cannot be compared with those of Figure 2 since differences in chloride concentration change the potentials of the reference electrode.

In all of the runs with organic reductants, a critical current density was reached, above which the potential rose to the value observed in the absence of the organic material. Potentials in this region fluctuated and the critical current density, at concentrations of 0.1 *M* or less, varied from 1 to 5 × 10^{-3} amp./cm.^{2}. Since the previous investigators[10] worked at current densities several orders of magnitude greater than ours, there must have been at least three reacting species being simultaneously oxidized under their experimental conditions, namely acetate ions, the acetic acid molecules, and the organic reductant. The concentration of unoxidized organic reactant must have been practically zero.

Conclusions

Since naphthalene is preferentially oxidized at the electrode, the formation of naphthyl acetate would proceed *via* the formation of a naphthalene radical ion, rather than an acetoxy radical. This is in agreement with the mechanism suggested by Eberson.[15]

The absence of methylnaphthalene and of anode gas, in any significant amounts, under the experimental conditions of Linstead[10] is probably due to the naphthalene being oxidized to the radical ion, which then reacts further at potentials below those required for the formation of acetoxy radicals. Further work is now in progress, on a preparative scale.

Acknowledgment.—We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for their generous support of this work. We wish also to thank the National Science Foundation for financial assistance to Miss Leung and to Mr. Herz, under the National Science Foundation Student Research Participation program. We wish also to thank Engelhardt Industries for their gift of several platinized titanium electrodes.

[15] L. Eberson, *Acta Chem. Scand.*, **17**, 2004 (1963).

Coumarin-3-carboxylic Acids

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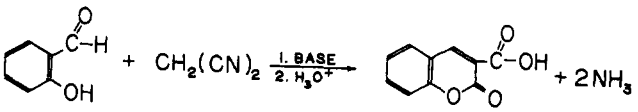
Although the method for preparing coumarin-3-carboxylic acids using basic catalysts has been known for a considerable number of years,[1,2] many of the simpler compounds have not been prepared, and none have been synthesized using malononitrile as one of the reactants in such a procedure.

In this report a procedure for the preparation of coumarin-3-carboxylic acids is given in which malononitrile is condensed with aldehydes or ketones in the presence of piperidine and described as method A. Three of the acids were also prepared by the Knoevenagel[1,2] procedure (method B) for comparison. The yields by our method (method A) are somewhat better than those of Knoevenagel which were in the range of 80%. The compounds prepared in the I–IV series are described in Table I.



Efforts were made to prepare the 4-phenyl derivative of IV by reacting 2,4-dihydroxybenzophenone with malononitrile, with diethyl malonate, and with malonic acid in the presence of piperidine. In all cases a reaction occurred, but either during the formation of the compound or during the hydrolysis the compound was decarboxylated, negating our attempt to ascertain what effect an electrophilic group in position 4 would exert on a powerfully fluorescent compound such as compound IV.

Of primary interest to us is the fluorescence of the coumarins, which in this series is most pronounced in compound IV. In view of the low but definite fluorescence levels in compounds I–III it appears that the conclusion of Seshadri[3] that a hydroxyl group must be present in a coumarin for it to fluoresce is in considerable error.

Table II gives the fluorescence in quinine reference units (g.r.u.), the ultraviolet absorption characteristics, and the *p*-bromophenacyl derivatives of the compounds of the I–IV series.

Experimental[4]

Preparation of Members of I–IV Series. Method A.—To a mixture consisting of 0.1 mole of malononitrile and 0.1 mole of the aldehyde or ketone was slowly added, with shaking, to 20 ml. of piperidine. If the mixture did not become hot and the mass become homogeneous, it was gently heated on a hot plate until homogeneity was obtained. The mixture, after cooling, was treated with 100 ml. of 6 *N* hydrochloric acid, chilled, and filtered. The precipitate was refluxed for 18 hr. in 100 ml. of 9 *N* hydrochloric acid. After chilling the mixture, it was filtered and the precipitate was dried in air.

Analytical samples were obtained either by recrystallizing the compounds twice from benzene–heptane mixtures or by dissolving the compound in ethyl acetate and then precipitating the compound with heptane. The process was repeated in either case for a second recrystallization.

Method B.—One-tenth of a mole of the aldehyde or ketone was mixed with 0.1 mole of diethyl malonate followed by 20 ml. of piperidine. The mixtures were warmed on a hot plate, if necessary, to produce complete solution of the reactants.

Acidification, hydrolysis, and purification of the compounds were effected in the same manner as in method A. Compounds which were prepared by both methods were proven to be identical by mixture melting points and by their infrared spectra.

Preparation of *p*-Bromophenacyl Derivatives of I–IV Series.—One gram each of the coumarin acid, 2′,4-dibromoacetophenone,

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[1] E. Knoevenagel, *Ber.*, **31**, 2619 (1898).

[2] E. Knoevenagel, *ibid.*, **37**, 4461 (1904).

[3] (a) S. Rangaswami and T. R. Seshadri, *Proc. Indian Acad. Sci.*, **12A**, 375 (1940); *Chem. Abstr.*, **35**, 3526 (1941). The reference in R. C. Elderfield's, "Heterocyclic Compounds," Vol. **2**, p. 193, is in error as to the year of publication of the above article. (b) See also C. E. Wheelock, *J. Am. Chem. Soc.*, **81**, 1348 (1959), on fluorescence in coumarins.

[4] Analyses were performed by Dr. Karl Tiedcke, 705 George Street, Teaneck, N. J. All melting points were taken on Fischer-Johns melting point blocks.