because of the increased facility for side-chain coordination. The specificity associated with the nitrating agent presents a more difficult problem. Perhaps solvent effects play an important role. In any case the differences are not surprising since analogous situations exist. Norman and Radda[15] remarked on the dissimilar *ortho–para* ratios obtained from the reactions of methyl phenethyl ether with mixed acid and nitric acid–acetic anhydride. To explain the high *ortho–para* ratio with nitric acid–acetic anhydride, the authors proposed an SN2 displacement followed by cyclic coordination.

Experimental

Nitration of Anisole with Nitronium Tetrafluoroborate.—Nitronium tetrafluoroborate was prepared from fuming nitric acid–hydrogen fluoride–boron trifluoride–nitromethane according to the method of Kuhn and Olah.[16]

A solution of nitronium tetrafluoroborate (0.05 mole) in tetramethylene sulfone (100 g.) was added during 5 min. to a stirred solution of anisole (0.5 mole) in tetramethylene sulfone (30 g.) at 21–24°. The reaction was terminated after the desired time span by dilution with water (300 ml.). The organic layer was diluted with ether (250 ml.), washed with water, and dried over calcium chloride. After evaporation of the ether, analysis was performed by gas chromatography on an Apiezon L (14% w./w.) column (12 ft., 200°, He flow rate of 80 cc./min.). In one reaction the amount of nonvolatile product, determined by distillation, was found to be 4% of the total product. The orientation data are recorded in Table II.

Nitration of Toluene with Nitronium Tetrafluoroborate.[6,11-13]—Nitration of toluene, as well as product analysis, was carried out under the same conditions as employed for anisole. The results are summarized in Table III.

Acknowledgment.—We are grateful to the National Science Foundation for support of this work.

[15] R. O. C. Norman and G. K. Radda, *J. Chem. Soc.*, 3030 (1961).

[16] S. J. Kuhn and G. A. Olah, *J. Am. Chem. Soc.*, **83**, 4564 (1961).

Some Electrochemical Oxidations in Anhydrous Acetic Acid

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In a recent publication,[1] Ross, Finkelstein, and Petersen suggested that aromatic hydrocarbons are anodically oxidized in anhydrous acetic acid, forming radical cations. Their argument is based primarily upon the analysis of the products of electrolysis in anhydrous acetic acid–potassium acetate solutions containing various added hydrocarbons, although they also reported that the discharge potential was lowered when naphthalene was added to a solution of potassium acetate in acetic acid. We have reported[2] direct evidence for the anodic oxidation of aromatic hydrocarbons in anhydrous acetic acid solutions, obtained by the measurement of anode potentials in the presence and in the absence of aromatic substrates. Under our conditions, naphthalene and anthracene were oxidized at potentials which were about 0.5 and 0.8 v. less anodic, respectively, than those required for the oxidation of acetic acid. Benzene did not oxidize under our conditions. We wish now to report the extension of our work to other classes of substrates.

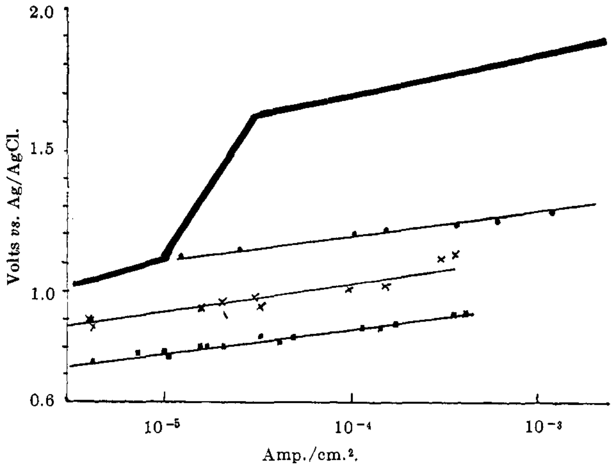

Figure 1.—Anode potential *vs.* current density (semilog scale): ●, naphthalene; ×, α-naphthyl acetate; and ■, anthracene.

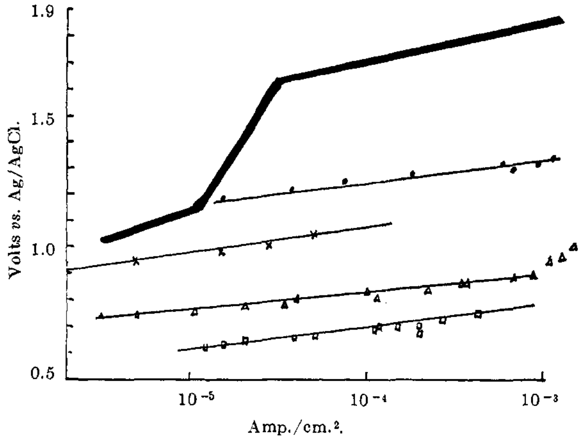

Figure 2.—Anode potential *vs.* current density (semilog scale): ●, phenyl methyl ether; ×, acetanilide; △, α-naphthyl methyl ether; and □, aniline.

Experimental

The apparatus and general procedure were those of the previous work.[2] Liquids were purified by distillation. Solids were recrystallized, when necessary, until the melting points agreed with those reported in the literature. The substrates were α-naphthyl methyl ether, phenyl methyl ether, α-naphthoquinone, α-naphthyl acetate, acetanilide, aniline, and mesitylene. The current densities ranged from 10^{-6} to 5×10^{-3} amp./cm.². Stationary state electrode potentials were measured against a Ag/AgCl(s) reference. The anode was a 1-cm.² piece of platinized titanium. As reported previously,[2] the results using the titanium-based platinum surface were in good agreement with those obtained using pure platinum. To avoid evolution of hydrogen, the cathode was a large Ag/AgCl(s) electrode. No attempts were made at product analysis. For any particular run, the data were reproducible within 25 mv., but repeat runs in fresh solution sometimes gave results that varied by as much as 60 mv. All solutions contained KOAc.

Results

Figures 1 and 2 show the variation of anode potential with current density, on semilog paper. (The previously published results with anthracene and naphthal-

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[1] S. D. Ross, M. Finkelstein, and R. C. Petersen, *J. Am. Chem. Soc.*, **86**, 4139 (1964).

[2] M. Leung, J. Herz, and H. W. Salzberg, *J. Org. Chem.*, **30**, 310 (1965).

ene are included for comparison.) The diffuse curve shown in each figure is a reference curve for the oxidation of acetic acid in the absence of added substrate. It was compiled from the results of eight runs, each in a fresh batch of solution. The descending portion of the hysteresis loop is not shown. The lower plateau is probably the region of acetate ion oxidation and the upper portion is probably that of oxidation of molecular acetic acid, as shown by the shift of the curve in the direction of higher currents when the concentration of acetate ion is increased.[2]

The straight lines shown are obtained on addition of oxidizable substrates. The Tafel equation[3a] is followed. The slopes are usually either 0.8–0.9 or 0.10–0.12, both indicating an irreversible electron transfer.[3b] In the case of α-naphthyl methyl ether, the slope was somewhat lower.

In each case of substrate oxidation, a limiting diffusion current density was reached, which was usually about 3–10 ma./cm.^{2}, depending on the concentration. In Figure 2, the data for α-naphthyl methyl ether show the trend toward higher potentials, starting at about 1 ma./cm.^{2}. By about 5 ma./cm.^{2}, the potentials would have risen to those of the acetic acid reference curve, if graphed. To avoid complicating the diagram, the results approaching the limiting diffusion current density are not shown for the other substrates.

Also not graphed are the results obtained using solutions to which benzene, mesitylene, and α-naphthoquinone had been added. In these cases, the reference curve was displaced slightly toward higher potentials, without significant change in shape. This indicates that the added substrates did not oxidize under the experimental conditions but were only adsorbed, decreasing the surface available for acetic acid oxidation. The shift toward higher potentials would therefore be due to an increase in the real (as opposed to apparent) current density.

Discussion and Conclusions

The graphs show that the ethers, the ester, the amide, the amine, and the polynuclear hydrocarbons investigated oxidize at potentials well below those required for the oxidation of molecular acetic acid.[4] The results of Table I, using 10^{-4} amp./cm.^{2} as a convenient reference current, show roughly that the more strongly *ortho–para*-directing substituents lower the oxidation potential more strongly, as would be expected. The potential differences are appreciable. Aniline, the extreme case, is oxidized at 1 v., or about 23 kcal., less than acetic acid. Even phenyl methyl ether, the least reactive of our oxidizable substrates, oxidizes at about 0.45 v. or 10 kcal. less than acetic acid. Unfortunately, since there are no data for reversible standard electrode potentials, our results cannot be used to calculate activation energies. As a guess at the order of magnitude of the activation energy, we can estimate the exchange current density, i_0, as being about 10^{-10} to 10^{-20} amp./cm.^{2}, for a very slow reaction.[5] (The exchange current is defined as the rate at which electrons are transferred back and forth between the oxidized and reduced forms of the reactants in the absence of an applied potential, *i.e.*, at equilibrium.) If so, since i_0 is defined as

$$i_0 = (f/N)(kT/h)C_s e^{-\Delta F^*/kT}$$

we can estimate ΔF^*, the free energy of activation. C_s, the surface concentration of substrate molecules may be estimated at 10^{14} (there are about 10^{15}–10^{16} metal atoms per cm.^{2}) and f, the Faraday, N Avogadro's number, k, the Boltzmann constant, h, Planck's constant, and T, the absolute temperature are known. If we neglect the entropy of activation, the enthalpy of activation would be about 20–30 kcal./mole. This would be much too small for the dissociation of the substrate into a radical and a hydrogen atom. The mechanism of reaction probably would therefore involve the formation of a radical cation. However, this is just a guess. We hope to study this matter further.

TABLE I

ANODE POTENTIALS AT 10^{-4} AMP./CM.^{2}

Compd.	Potential, v.
Acetic acid	1.70 ± 0.03
Phenyl methyl ether	1.25
Naphthalene	1.2
Acetanilide	1.1
α-Naphthyl acetate	1.0
Anthracene	0.86
α-Naphthyl methyl ether	0.82
Aniline	0.70

We can form no judgment on the argument advanced by Ross, Finkelstein, and Petersen, since they worked under different conditions. Their current densities were two orders of magnitude above that of the limiting diffusion current, *i.e.*, their currents were much greater than the rate of diffusion of substrate molecules to the electrode surface. Also, the complications introduced by the probable diffusion of hydrogen to the anode and of anode products to the cathode makes interpretation of their results somewhat difficult. However, we would expect that since they greatly exceeded the limiting current density, large numbers of acetoxy radicals would be formed, in addition to organic cation radicals. There would therefore be several simultaneous processes occurring.

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(3) (a) E. C. Potter, "Electrochemistry, Principles and Applications," Cleaver-Hume Press, London, 1956, pp. 128, 133. The Tafel equation originally referred to the hydrogen evolution reaction but the term has *come to mean* any linear voltage–log current density equation. (b) J. O'M. Bockris and E. C. Potter, *J. Electrochem. Soc.*, **99**, 181 (1952). These authors work out the slope of the Tafel plot to be expected from various mechanisms. The slope is given by the expression $RT/\beta\lambda f$, where R is the gas constant, T is the Kelvin temperature, f is the Faraday, β is the transfer coefficient, *i.e.*, the fraction of the potential assisting the rate determining step, and λ is the number of electrons transferred in all the processes leading up to and including the rate-determining step. For a slow primary electron transfer, $\lambda = 1$, $\beta \approx 1/2$, and the Tafel slope, at 25°, is about 0.12. For a reversible one-electron step, both β and $\lambda = 1$ and the Tafel slope is 0.03. For a reversible, two-electron step, the Tafel slope is 0.06. For a reversible electron transfer followed by a second, irreversible transfer, $\lambda = 2$, $\beta \approx 3/4$, and the slope should be about 0.08. Obviously, no conclusion can be reached from the slopes of the graphs reported here other than to say that they indicate that the processes are probably not reversible.

(4) L. Eberson and K. Nyberg [*Acta Chem. Scand.*, **18**, 1568 (1964)], in an article published while this manuscript was in the hands of the reviewers, *have reported the formation of* acetoxynaphthalene *and o- and p*-acetoxyanisole, in 30–40% yields by anodic oxidation of the parent compound in acetic acid–water–potassium acetate solutions. The potential was 1.5 v., which is less than that required for the Kolbe reaction.

(5) See ref. 3a, p. 130.

Acknowledgment.—We wish to thank the Petroleum Research Fund, administered by the American Chemical Society, for the support of this project and the National Science Foundation for assistance to Miss Leung, under the National Science Foundation Student Participation Program.

2-Benzo[*b*]thien-2-yl-1,3,3-trimethyl-2-indolinecarbonitrile

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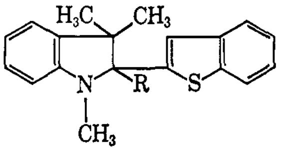
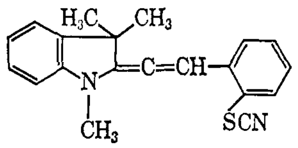
1,3,3-Trimethyl-2-methyleneindoline and 2-thiocyanatobenzaldehyde combine to give a material which herein is shown to be the title compound (Ia); thus the reaction involves the formation of a thianaphthene ring under unusually mild conditions.



Ia, R = CN
b, R = OH



II

The infrared spectrum of Ia shows no absorption attributable to NH, SH, C=C=C, C≡C, C≡N, SC≡N, N⇄C, or C=N=S groups. This eliminates from further consideration the allenic[1] structure II.

The n.m.r. spectrum of Ia shows three N–Me protons as a singlet at 2.93 p.p.m. (indicating that the nitrogen atom bears little or no formal positive charge),[3] six CMe_2 protons as two singlets at 1.03 and 1.68 p.p.m. (suggesting that the adjacent atom bears two different substituents),[3] a multiplet of eight aromatic protons at 6.5–8.0 p.p.m., and one proton as a singlet at 7.65 p.p.m.

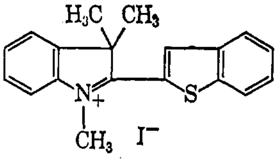
Structures containing the cyano group remained under consideration, for the lack of CN absorption in the infrared might possibly be attributed to the presence of the sulfur atom. Cyano absorptions are sometimes strongly attenuated by a nearby oxygen atom.[4] We therefore sought chemical evidence regarding the presence of a cyano group. The hydroxamic acid test for nitriles[5] was indeterminate. A solution of Ia in methanol saturated with hydrogen chloride slowly deposited ammonium chloride and gave after neutralization a material (Ib) with the empirical formula $C_{19}H_{19}NOS$ rather than the C_{21} products corresponding to the anticipated changes CN → CO_2Me or C(=NH)OMe. When the reaction was repeated using ethanol, the same C_{19} product was obtained. The hydroxamic acid test for esters[5] was negative when applied to Ib. That Ib was not an ordinary or imino ester was further shown by its infrared spectrum, which exhibits no C=O, C=NH, or N—H absorption, but does exhibit O—H absorption.

The n.m.r. spectrum of Ib is similar to that of Ia, but shows, in addition, a one-proton singlet at 2.60 p.p.m. attributable to an OH group. The ultraviolet spectrum of Ib in neutral ethanol is very similar to that of Ia; in acidic ethanol the absorptions change markedly, and both Ib and Ia have identical spectra.

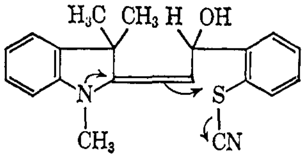
An alcoholic solution of either Ib or Ia gave red crystals (III) upon treatment with hydriodic acid. The n.m.r. spectrum of III shows N–Me at 4.66 p.p.m. (suggesting that the nitrogen atom bears a formal positive charge)[3] and a single (6H) C–Me absorption at 1.89 p.p.m.

The only reasonable structures for Ia, Ib, and III that accommodate the data are those shown, which incorporate a thianaphthene nucleus. These structures were confirmed by synthesis. The reaction between 2-thianaphthenyllithium and 1,3,3-trimethyloxindole gave Ib, which was converted to III. A solution of III when treated with potassium cyanide gave Ia.

A possible route for the formation of Ia may involve the cyclization and dehydration of IV to the ion III (as the cyanide), which reverts to the covalent form Ia, as in the synthesis above.



III



IV

An example of the formation of a thianaphthene ring by intramolecular displacement of cyanide from a thiocyanate is known,[6] but it requires strongly basic conditions.

Experimental[7]

2-Benzo[*b*]thien-2-yl-1,3,3-trimethyl-2-indolinecarbonitrile (Ia).—A solution of 3.26 g. (0.02 mole) of *o*-thiocyanatobenzaldehyde[8] and 3.46 g. (0.02 mole) of 1,3,3-trimethyl-2-methyleneindoline in 200 ml. of ethanol was refluxed 1 hr., concentrated *in vacuo*, and chilled to give 4.92 g. (77%) of crude Ia, m.p. 154–169°. Recrystallization from ethanol with Norit treatment gave material of m.p. 161.0–164.0° (further recrystallizations from ethanol or benzene did not narrow this range): ultraviolet, $\lambda\lambda_{\max}^{\mathrm{EtOH}}$ mμ (ϵ) 229 (35,000), 258 (17,000), 266 (14,900), 291 (6350), 301 (4800); $\lambda\lambda_{\max}$ (EtOH saturated with dry HCl) mμ (ϵ) 248 (11,500) 378 (26,800); n.m.r., see discussion; infrared, 1610 (s), 1485 (s),

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[1] Allenes are reported[2] to be formed by the condensation of heterocyclic methylene bases with aromatic aldehydes. They were unstable and reactive, and their structures have not been confirmed by spectral evidence.

[2] W. H. Mills and R. Raper, *J. Chem. Soc.*, **127**, 2466 (1925).

[3] See Experimental.

[4] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1958, p. 266.

[5] R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 4th Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p. 123.

[6] F. Arndt, A. Kirsch, and P. Nachtwey, *Ber.*, **59**, 1074 (1926).

[7] Analyses are by Galbraith Laboratories, Knoxville, Tenn.; melting points are corrected, taken on a Thomas–Hoover apparatus; infrared spectra were measured on a Perkin-Elmer Infracord 137 in $CHCl_3$ solvent, positions of sharp absorption maxima given in reciprocal centimeters followed by relative intensities: s = strong, m = medium, w = weak; ultraviolet spectra were run on a Beckman DK-1; n.m.r. spectra were measured on a Varian A-60 in $DCCl_3$ solvent, with TMS reference, shifts are given in parts per million followed in parentheses by the relative integrated intensity and the multiplicity: s = singlet, m = multiplet. We thank Dr. D. P. Hollis of Varian Associates and Mr. F. E. Dickson of NMR Specialties, Inc., for obtaining and interpreting the n.m.r. spectra.

[8] P. Friedlaender and E. Lenk, *Ber.*, **45**, 2083 (1912).