tionalized by means of a kinetic law such as

$$\frac{\mathrm{d}[\mathrm{PhCl}]}{\mathrm{d}t} = \left[\frac{\phi I_a}{k_3}\right]^{1/2}\left[\frac{a + b[\mathrm{PhBr}]^n}{c + e[\mathrm{PhBr}]^n}\right]^m \times [\mathrm{PhBr}]\{k_1[\mathrm{Cl_2}] + k_2[\mathrm{BrCl}]\}$$

Thus, when the concentration of bromobenzene is small the rate would be proportional to a/c, and when bromobenzene concentration is large the rate would be proportional to b/e. Any number of schemes leading to such a law suggest themselves, but their consideration without additional data does not seem appropriate.

Acknowledgment. We wish to thank Brown University for computer time when B. M. was visiting there on sabbatical leave.

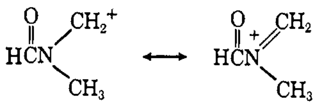
Anodic Oxidations. IV. The Electrochemical Oxidation of the Side Chain of Mesitylene and Toluene in Acetic Acid

Sidney D. Ross, Manuel Finkelstein, and Raymond C. Petersen

Contribution from the Research and Development Center, Sprague Electric Company, North Adams, Massachusetts 01247. *Received March 28, 1967*

Abstract: The electrochemical oxidation of mesitylene and toluene in acetic acid containing tetramethylammonium nitrate results almost exclusively in substitution of the side chain rather than the ring. These products include the benzyl nitrates, the benzyl acetates, and the bibenzyls as well as further oxidation products, benzaldehydes, and benzal diacetates. Evidence is presented in support of a mechanism in which the first two steps are: (1) discharge of a nitrate ion to give a nitrate radical, and (2) hydrogen abstraction by the nitrate radical on the aromatic substrate to give a benzyl radical.

When N,N-dimethylformamide is oxidized anodically in acetic acid containing acetate ion, it is the amide rather than acetate ion which is oxidized at the electrode in the primary step.[1,2] When the anodic acetoxylation is carried out in acetic acid containing ammonium nitrate, nitrate ion is oxidized in the primary anodic process.[3] Both reactions lead to the same product, N-acetoxymethyl-N-methylformamide, since in both reactions the product-forming intermediate is almost certainly the cation, I. The essential difference between the two systems is not in the nature of the product but in the manner in which I is generated.



I

In the electrochemical acetoxylation of alkyl-substituted aromatic hydrocarbons, *e.g.*, ethylbenzene and mesitylene, the primary anodic process is again the oxidation of the hydrocarbon rather than acetate ion.[2,4] The reaction is a complex one, since discharge of acetate ion accompanies the anodic oxidation of the hydrocarbon. The total product contains both ring- and side-chain-substituted acetoxylation products as well as ring- and side-chain-substituted methylation products. Nevertheless, the predominant reaction mode is acetoxylation, with substitution on the ring.

If such substrates could be electrochemically reacted in a system such that an anion, *e.g.*, nitrate ion, is oxidized at the anode in the primary step in preference to the hydrocarbon, one might hope to find the product composition significantly altered. In particular one might hope to eliminate the methylation products and find that the major site of attack is now the side chain rather than the ring. The present study was designed to explore this possibility by investigating the anodic oxidation of mesitylene and toluene in acetic acid containing tetramethylammonium nitrate.

Results

When a solution of mesitylene (10 ml) and tetramethylammonium nitrate (0.05 mole) in glacial acetic acid (50 ml) is electrolyzed at a current of 400 ma, the only gaseous product produced is hydrogen, and it is formed at almost exactly the theoretical rate of 1 mole of hydrogen per 2 faradays of charge passed through the solution.[5] To determine the nongaseous products formed in this reaction the electrolysis was run in the larger apparatus described in the Experimental Section. In this experiment a solution of mesitylene (0.144 mole) and tetramethylammonium nitrate (0.20 mole) in glacial acetic acid (160 ml) was electrolyzed at 2.0 amps until 2.02 equiv of charge per mole of mesitylene was passed through the solution. The products, determined by vpc, are listed in Table I.

The products listed in Table I account for more than 55% of the starting mesitylene. In addition it was possible to isolate, by a combination of molecular distillation and column chromatography, a sufficient amount of 3,3′,5,5′-tetramethylbibenzyl to unequivocally establish its presence in the reaction mixture.

---

[1] S. D. Ross, M. Finkelstein, and R. C. Petersen, *J. Org. Chem.*, **31**, 128 (1966).

[2] L. Eberson and K. Nyberg, *J. Am. Chem. Soc.*, **88**, 1686 (1966).

[3] S. D. Ross, M. Finkelstein, and R. C. Petersen, *ibid.*, **88**, 4657 (1966).

[4] S. D. Ross, M. Finkelstein, and R. C. Petersen, *ibid.*, **86**, 4139 (1964).

[5] For a description of the apparatus and procedure used in this determination see ref 4.

Table I. Nongaseous Products from Mesitylene Electrolyzed in the Presence of Tetramethylammonium Nitrate

	Mole
Mesitylene	0.0523
3,5-Dimethylbenzyl acetate	0.0130
3,5-Dimethylbenzyl nitrate	0.0132
3,5-Dimethylbenzaldehyde	0.0018
2,4,6-Trimethylphenyl acetate	<0.0003

The above products are to be compared with those previously obtained[4] when a solution of mesitylene (0.075 mole) and potassium acetate (0.0509 mole) in glacial acetic acid (60 ml) was electrolyzed for 28 hr at a current of 400 ma. These earlier results are repeated in Table II.

Table II. Nongaseous Products from Mesitylene Electrolyzed in the Presence of Potassium Acetate

	Mole
Mesitylene	0.0425
2,4,6-Trimethylphenyl acetate	0.00947
3,5-Dimethylbenzyl acetate	0.00376
5-Ethyl-*m*-xylene	0.0022
Isodurene	0.00078

In a study of the gas generated during electrolysis of a solution of toluene (10 ml) and tetramethylammonium nitrate (0.05 mole) in glacial acetic acid (50 ml) at a current of 400 ma, it was again found that the only gas produced was hydrogen.[5] The nongaseous products, obtained after a solution of toluene (0.188 mole) and tetramethylammonium nitrate (0.2 mole) in glacial acetic acid (160 ml) had been electrolyzed at 2.0 amps until 2.25 equiv of charge per mole of toluene had been passed through the solution, were determined by vpc and are shown in Table III.

Table III. Nongaseous Products from Toluene Electrolyzed in the Presence of Tetramethylammonium Nitrate

	Mole
Toluene	0.0231
Benzaldehyde	0.0070
Benzyl acetate	0.0188
Benzyl alcohol and benzyl nitrate	0.0096–0.0136
Benzylidene diacetate	0.0007
Bibenzyl	0.0011

Under the vpc conditions used for the above analyses benzyl acetate and *p*-acetoxytoluene had identical retention times and were not distinguishable. The hydrolysis products, benzyl alcohol and *p*-cresol, are, however, readily distinguishable. After hydrolysis the electrolysis product contained 0.0285 mole of benzyl alcohol and no detectable quantity of *p*-cresol. The product originally present was, therefore, benzyl acetate and not *p*-acetoxytoluene.

The retention times for benzyl alcohol and benzyl nitrate were not sufficiently separated to permit their individual determination. It was possible to estimate the sum of these two components, and in Table III the numbers given are for the extreme possibilities, all alcohol or all nitrate. The actual value is somewhere between these two extremes.

The previous study[4] of the oxidation of aromatic hydrocarbons in acetic acid containing acetate ion did not include toluene. For comparison with the above study with nitrate ion, a solution of toluene (0.056 mole) and potassium acetate (0.061 mole) in acetic acid (48 ml) was electrolyzed at 400 ma for 38.5 hr. The products formed were not determined quantitatively but were shown to be *o*-acetoxytoluene, benzyl acetate, and *p*-acetoxytoluene, with *o*-acetoxytoluene being the major product and the combined amount of *o*-acetoxytoluene and *p*-acetoxytoluene being significantly larger than the amount of benzyl acetate. Since *p*-acetoxytoluene and benzyl acetate had the same retention time, the product mixture was hydrolyzed to give *o*-cresol, benzyl alcohol, and *p*-cresol, a mixture which proved separable by vpc.

Experimental Section

Apparatus. The electrolysis cell was a water-jacketed cylinder, 13.5 cm in length and 4.5 cm in diameter. Two outer joints, one 45/50 and one 24/40, were sealed to the top of the cell chamber. The two platinum electrodes, 9 × 3 cm at a separation of 1.5 cm, were sealed in a 45/50 inner joint and positioned in the cell such that the electrodes extended to within 2.5 cm of the bottom of the cell chamber. The 24/40 joint was fitted with a reflux condenser, and the whole system was protected from the atmosphere with a drying tube. A magnetic stirrer was used to mix the electrolysis solution.

Determination of Nongaseous Products. At the end of the electrolysis the cell contents were poured into 1 l. of water. This mixture was extracted with four 200-ml portions of ether; the combined ether extracts were neutralized by stirring with a suspension of sodium bicarbonate in water. The ether was separated, and the remaining suspension was extracted with ether. The combined ether extracts were dried over magnesium sulfate and concentrated through a Vigreux column. For analysis the residue was diluted to 100 ml with ether.

The ether solutions were analyzed by vpc using a Perkin-Elmer large diameter Golay column of 0.06-in. i.d. and 300-ft length in which the stationary phase was Ucon polyglycol LB-550-X. The unknown solutions were compared with standards prepared from the identified components.

Materials. Mesitylene was twice distilled at atmospheric pressure, only middle cuts being taken each time; bp 160–161°. The toluene and glacial acetic acid were both ACS reagent grade from the General Chemical Co. and were used without purification. Analyzed, reagent grade potassium acetate was obtained from the J. T. Baker Chemical Co.

Tetramethylammonium nitrate was prepared by neutralizing a 20% solution of tetramethylammonium hydroxide in methanol with dilute nitric acid. The solvents were removed, and the crude product was twice crystallized from methanol containing a little ether; yield, 91%.

Anal. Calcd for $C_4H_{12}N_2O_3$: C, 35.29; H, 8.88; N, 20.58. Found: C, 35.41; H, 8.91; N, 19.89.

Materials Used in Preparing Standards. The preparation and properties of 3,5-dimethylbenzyl acetate and 2,4,6-trimethylphenyl acetate (acetoxymesitylene) have been reported previously.[4]

3,5-Dimethylbenzyl nitrate was prepared by the reaction of 3,5-dimethylbenzyl bromide and silver nitrate in acetonitrile;[6] yield, 54%; bp 58–60 (0.25 mm); $n^{22}\mathrm{D}$ 1.5172.

Anal. Calcd for $C_9H_{11}NO_3$: C, 59.66; H, 6.12; N, 7.73. Found: C, 60.16; H, 6.21; N, 7.22.

3,5-Dimethylbenzaldehyde was obtained in 71% yield by adding the above nitrate to a refluxing solution of a small amount of concentrated sulfuric acid in acetic acid; bp 35–36° (0.015 mm); $n^{22}\mathrm{D}$ 1.5405. The details of this reaction will be published elsewhere.

p-Acetoxytoluene and *o*-acetoxytoluene were prepared by treating the appropriate cresol with acetic anhydride and pyridine. The former had bp 97° (13 mm) and $n^{23}\mathrm{D}$ 1.4990. The latter had bp 87–90° (13 mm) and $n^{22.5}\mathrm{D}$ 1.4975.

---

(6) A. F. Ferris, K. W. McLean, I. G. Marks, and W. D. Emmons, *J. Am. Chem. Soc.*, 75, 4078 (1953).

Bibenzyl was obtained from Distillation Products Industries and benzylidene diacetate was obtained from Aldrich Chemical Co., Inc. Benzyl nitrate was prepared by a published procedure.[6]

Isolation of 3,3′,5,5′-Tetramethylbibenzyl. The solvent was removed from the vpc analysis solution for the mesitylene electrolysis. The residue was distilled first at the water pump with the bath temperature at 140° (0.02 mm) until the head temperature was 67°. The dark residue from these distillations was distilled through a short-path still, and the viscous, clear, amber distillate was dissolved in benzene and chromatographed on alumina. The first two elution fractions gave a small amount of oil which was crystallized from ethanol to yield 29 mg of white crystals; mp 62–70°. After sublimation and crystallization from methanol the melting point was raised to 70–73°. A mixture melting point with authentic 3,3′,5,5-tetramethylbibenzyl, prepared by the procedure of Weiler,[7] was undepressed.

Discussion

Anodic oxidation of a solution of mesitylene in acetic acid containing tetramethylammonium nitrate results in products which are significantly different from those observed with potassium acetate present in lieu of the nitrate. This is apparent from the results reported in Tables I and II. With the nitrate salt only a trace of the product, approximately 1%, involves substitution of the aromatic ring. The remaining products all result from an attack on the side chain rather than the ring, and no methylation products were detected.

In the electrochemical oxidation with potassium acetate present, 18.4% of the isolated product is the result of a methylation reaction, and the remaining 81.6% is due to acetoxylation. Of this acetoxylation product, 71.6% is the result of substitution in the ring to give 2,4,6-trimethylphenyl acetate, and 28.4% of the acetoxylation is on the side chain to give 3,5-dimethylbenzyl acetate. The major reaction mode is, thus, acetoxylation of the ring.

Comparable results were observed with toluene. In the presence of potassium acetate the major reaction mode is again ring acetoxylation to give *o*- and *p*-acetoxytoluene. With tetramethylammonium nitrate present all of the observed products (Table III) resulted from an attack on the side chain rather than the ring.

More significantly, in the oxidation of both mesitylene and toluene in the presence of the nitrate the coupling products, 3,3′,5,5′-tetramethylbibenzyl and bibenzyl, are definitely present in the product mixtures. The presence of these two hydrocarbons constitutes unambiguous proof for the generation of some 3,5-dimethylbenzyl radical in the former reaction and of benzyl radical in the latter reaction.

It is clear that the substitution of tetramethylammonium nitrate for potassium acetate in these anodic oxidations results in a change in both the reaction products and the reaction mechanism. The anodic, ring acetoxylation reaction has now been extensively studied,[1,2,8] and its mechanism is well understood. The reaction commonly occurs *via* electron transfer from the organic substrate to the anode, forming an electrophilic species, and the products result from ionic intermediates.

In the oxidations with the nitrate present some of the reactions involve radical rather than ionic intermediates. This must be the case for the formation of the bibenzyls, since these products almost certainly result from discharge of nitrate ion followed by hydrogen abstraction and coupling as shown below.

$$NO_3^- \longrightarrow e + NO_3\cdot \qquad (1)$$

$$NO_3\cdot + RCH_3 \longrightarrow HNO_3 + RCH_2\cdot \qquad (2)$$

$$2RCH_2\cdot \longrightarrow RCH_2CH_2R \qquad (3)$$

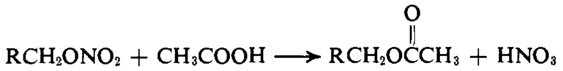
A previous study from this laboratory[3] has shown that nitrate ion has a relatively low discharge potential. The present experiments point to reaction 1 as the primary electrode process, *i.e.*, a one-electron transfer from nitrate ion to the anode to give the nitrate radical, a species previously observed as a primary product in the decomposition of nitrogen pentoxide.[9,10]

The steps leading to the formation of the benzyl nitrates are less certain than those accounting for the genesis of the bibenzyls. One possibility is the coupling of a benzyl radical formed by (2) with a nitrate radical produced in (1). An alternate possibility is the further anodic oxidation of a benzyl radical, as shown in (4),

$$RCH_2\cdot \longrightarrow e + RCH_2^+ \qquad (4)$$

to give a benzyl carbonium ion which then can react either with nitrate ion to give the benzyl nitrate or with acetate ion to give the benzyl acetate.

The benzyl acetates obtained do not arise from coupling of benzyl radicals with acetoxyl radicals. The absence of gas generation at the anode and the failure to detect any methylation products as well as the recognized instability of the acetoxyl radical all support this conclusion. One possible path to the benzyl acetates has already been described. The benzyl acetates might also arise from an acetolysis reaction on the benzyl nitrates as shown in (5).



$$RCH_2ONO_2 + CH_3COOH \longrightarrow RCH_2O\overset{\overset{O}{\|}}{C}CH_3 + HNO_3 \qquad (5)$$

This reaction does, in fact, occur. When a solution of benzyl nitrate (5 ml) in acetic acid (15 ml) is refluxed 2.5 hr, 25% of the nitrate is converted to acetate. In the electrochemical oxidation of mesitylene almost equivalent quantities of 3,5-dimethylbenzyl nitrate and 3,5-dimethylbenzyl acetate were obtained. It is improbable that the acetolysis reaction is responsible for such extensive conversion of nitrate to acetate at the much lower temperatures (40° or below) of the anodic oxidations. It follows, therefore, that reaction 4 does occur in these systems and that both benzyl radicals and benzyl carbonium ions are product-forming intermediates.

Similarly, the small amount of benzyl alcohol observed in the oxidation of toluene could arise from hydrolysis of the acetate or nitrate or from hydration of the benzyl carbonium ion, all by traces of water in the system. The remaining products, the benzaldehydes and benzal diacetates, are secondary products arising from the further oxidation of the products already discussed.

The most significant aspect of these results is the very striking preference shown by these reactions with the

---

(7) M. Weiler, *Ber.*, 33, 338 (1900).

(8) M. Leung, J. Herz, and H. W. Salzberg, *J. Org. Chem.*, 30, 310 (1965); H. W. Salzberg and M. Leung, *ibid.*, 30, 2873 (1965).

(9) H. S. Johnston, *J. Am. Chem. Soc.*, 75, 1567 (1953).

(10) G. Schott and N. Davidson, *ibid.*, 80, 1841 (1958).

nitrate salt present for substitution on the side chain rather than on the ring. This is, *per se*, almost compelling evidence for a mechanism including a step in which a radical abstracts a hydrogen atom from the aromatic substrate, and, in fact, all of the observed products can be conveniently rationalized from this point of departure.[11]

---

(11) For a similar interpretation of the anodic methoxylation of alkylbenzenes, see, K. Sasaki, H. Urata, K. Uneyama, and S. Nagaura, *Electrochim. Acta*, 12, 137 (1967).

Electrochemiluminescence of Aryl-Substituted Isobenzofurans, Isoindoles, and Related Substances[1]

Arnold Zweig, Gerlinde Metzler, Arthur Maurer, and Bernard G. Roberts

Contribution from the American Cyanamid Company,
Chemical and Research Service Departments, Central Research Division,
Stamford, Connecticut 06904. *Received March 1, 1967*

Abstract: The electrochemiluminescence emission, polarographic half-wave oxidation and reduction potentials, anion- and cation-radical stabilities, fluorescence spectra, and fluorescence efficiencies of a number of aryl-substituted isobenzofurans, isoindoles, and similar compounds have been examined in N,N-dimethylformamide solution. These data, together with molecular orbital calculations, permit several types of structure–property comparisons to be made which provide insight into the factors which affect ion-radical stability and electrochemiluminescence.

Electrochemiluminescence (ecl) may be defined as a process in which molecules capable of luminescing are raised to an excited electronic state by electrochemical energy. Of those *fluorescent* aromatic hydrocarbons which luminesce on successive electrochemical oxidation and reduction steps at platinum electrodes in polar aprotic media, rubrene (5,6,11,12-tetraphenyltetracene) has been found to emit the brightest visible light for the longest period.[2,3] The duration of this electrochemiluminescence under standardized conditions (*cf.* Experimental Section) is at best a matter of hours, and at the end of the emission period the fluorescer is found to be consumed. Purification of the components of the system and rigorous exclusion of air and moisture afford some small improvement in the brightness-duration characteristics; however, it is apparent that some factor intrinsic to the ecl process remains responsible for the consumption of material. The electrochemical processes at the electrodes produce ion radicals and these must be involved in the eventual production of excited singlets. The ion radicals and the excited state of the molecule are thus implicated as possible sources for degradation of the fluorescer. Attempted photolysis of several highly fluorescent and electrochemiluminescent molecules showed them to be quite photostable in the absence of oxygen.[4] Investigation of the contents of an exhausted rubrene ecl cell showed the presence of pseudorubrene,[5] a compound which had been previously reported as being formed on acid treatment of rubrene.[6] Since the cation radical of rubrene is known to be unstable in the solvent employed, N,N-dimethylformamide,[2,3] it appears that rearrangement of the rubrene cation to a pseudorubrene cation competes with the process leading to emission.

The report by Bergmann and co-workers[7] that 1,4,5,8-tetraphenylnaphthalene is a fluorescent compound which does not undergo rearrangement under the acid conditions which are responsible for the rubrene rearrangement prompted us to repeat their preparation of this compound. The synthesis involves Diels–Alder condensation of 1,4-diphenyl-1,3-butadiene with 1,2-dibenzoylethylene, aromatization of the cyclohexene adduct, and ring closure of the resulting *o*-diaroylbenzene to 1,3,4,7-tetraphenylisobenzofuran. Diels–Alder reaction of the isobenzofuran with acrolein, followed by treatment of the adduct with anhydrous hydrochloric acid, led to 1,4,5,8-tetraphenylnaphthalene-2-carboxaldehyde which was readily decarbonylated to produce the desired hydrocarbon. The latter is indeed a good electrochemiluminescent compound with a considerably longer ecl emission lifetime than rubrene under comparable conditions. Its ecl properties have previously been reported.[8] It was found that an intermediate in this synthesis, 1,3,4,7-tetraphenylisobenzofuran, an intensely green fluorescer, electrochemiluminesced with a brightness which was orders of magnitude greater than that of the hydrocarbons under the same conditions. Furthermore, the emission from the isobenzofuran endured for longer periods under comparable conditions. This finding resulted in an investigation of the chemical and physical variables involved in the ecl emission from isobenzofurans and related substances. In this paper we report on the effects of variation of fluorescer structure on the emission and

---

(1) A preliminary account of part of this work has been published: A. Zweig, G. Metzler, A. Maurer, and B. G. Roberts, *J. Am. Chem. Soc.*, **88**, 2864 (1966).

(2) D. L. Maricle and A. Maurer, *ibid.*, **89**, 188 (1967).

(3) M. M. Rauhut, D. L. Maricle, *et al.*, Technical Reports No. 4 and 5 to the Office of Naval Research and Advanced Research Projects Agency, Contract Nonr 4200(00), July 1964, AD 602,272, AD 606,989.

(4) A. Zweig, unpublished observations.

(5) D. L. Maricle and A. H. Maurer, unpublished observations.

(6) C. Moureu, C. Dufraisse, and G. Berchet, *Compt. Rend.*, **185**, 1085 (1927); C. Moureu, C. Dufraisse, and L. Enderlin, *ibid.*, **188**, 673 (1929); C. Dufraisse and G. Amiard, *ibid.*, **220**, 695 (1945).

(7) E. D. Bergmann, S. Blumberg, P. Bracha, and S. Epstein, *Tetrahedron*, 20, 195 (1964).

(8) A. Zweig, A. H. Maurer, and B. G. Roberts, *J. Org. Chem.*, **32**, 1322 (1967).