maximum over-all rate, $-d[\mathrm{As(III)}]/dt$, possible at any point in solution is approximately 7 mol l.$^{-1}$ sec^{-1}, and the maximum rate of loss of H_3AsO_3 is 2.8 mol l.$^{-1}$ sec^{-1}.

Chemical kinetic evidence obtained by other methods[19,20] supports the conclusion that reactions 12 and 13 are not rate limiting under our experimental conditions. The forward rate of reaction 12 can be estimated from other hydroxyl-weak uncharged acid reactions. Eigen and Maass[19] report that the forward constant for the reaction

$$OH^- + C_6H_5OH \underset{}{\overset{k_f}{\rightleftharpoons}} H_2O + C_6H_5O^-$$

is 1.4×10^{10} l. mol^{-1} sec^{-1} at 25°. The corresponding rate for reaction 12 is probably somewhat faster since H_3AsO_3 has three potentially acidic protons. Hence, we estimate the forward rate constant for reaction 12 to be approximately 4×10^{10} l. mol^{-1} sec^{-1}. Thus, the maximum rate possible for the disappearance of H_3AsO_3 for $a_{H^+} = 2.14 \times 10^{-9}\ M$, is approximately 73 mol l.$^{-1}$ sec^{-1}.

The forward and reverse rate constant for the I_3^- dissociation, reaction 13, have been determined by Myers[20] using nmr data. At 35°, he reports $k_f = (7.6 \pm 0.8) \times 10^7$ sec^{-1} and $k_b = (4.1 \times 0.4) \times 10^{10}$ l. mol^{-1} sec^{-1}. Considering the magnitude of these rates, the minor difference in temperature between his and our experiments can be neglected, and it is clear that the I_3^- equilibrium is readily established. Thus, the assumption that reactions 10 and 11 are not rate limiting is valid within experimental error for our experimental conditions.

The experimental value for k is a factor of approximately 30 less than the value obtained for k'. Reaction 12 is an anion–anion reaction while reaction 13 is between an anion and a neutral species, and it seems likely that the difference in k and k' is a result of electrostatic repulsion.

Schenk[21] has suggested a sequence of steps for the I_2–As(III) reaction in alkaline media without discussing the rate-determining step (eq 21–23). A similar

$$\text{I–I} + \text{:As(OH)}_2\text{O}^- \rightleftharpoons \text{I}^- + \text{I–As(OH)}_2\text{O} \qquad (21)$$

$$\text{I–As(OH)}_2\text{O} + \text{OH}^- \rightleftharpoons \text{I–As(OH)}_3\text{O}^- \qquad (22)$$

$$\text{I–As(OH)}_3\text{O}^- + 2\text{OH}^- \rightleftharpoons \text{I}^- + \text{As(OH)O}_3{}^{2-} \qquad (23)$$

reaction sequence can be written for the I_3^-–As(III) reaction. Our data indicate that the decomposition of the products formed by the electrolytic attack of I_2 and I_3^- upon :As(OH)$_2$O$^-$ is the rate-limiting step, *i.e.*

$$\text{I}_2 + \text{:As(OH)}_2\text{O}^- \rightleftharpoons \text{I}_2\text{–As(OH)}_2\text{O}^- \longrightarrow \text{products} \qquad (24)$$

$$\text{I}_3^- + \text{:As(OH)}_2\text{O}^- \rightleftharpoons \text{I}_3\text{–As(OH)}_2\text{O}^{2-} \longrightarrow \text{products} \qquad (25)$$

Acknowledgment. This work was supported by a grant from the University of Minnesota Space Sciences Center under a grant from NASA.

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[19] M. Eigen and G. Maass, "Technique of Organic Chemistry," Vol. VIII, Part II, Interscience Publishers, New York, N. Y., 1963, p 1035.

[20] O. E. Myers, *J. Chem. Phys.*, **28**, 1027 (1958).

[21] G. H. Schenk, *J. Chem. Educ.*, **41**, 32 (1964).

Anodic Oxidations of Aromatic Amines. III. Substituted Anilines in Aqueous Media[1]

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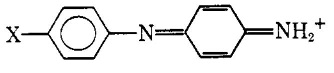
Contribution from the Department of Chemistry, University of Kansas, Lawrence, Kansas 66044. Received June 3, 1968

Abstract: The anodic oxidation of a series of *para*-substituted anilines in aqueous media revealed a common pattern of *para*-group elimination and head-to-tail coupling to give 4′-substituted 4-aminodiphenylamines. These products were identified by electrochemical, spectroscopic, and quantitative chemical methods.

In anodic oxidations of aromatic compounds, chemical reactions following electron transfer dominate the over-all electrode process. We have concentrated on this aspect of anodic processes, especially as applied to aromatic amines, in an attempt to establish a general pattern of behavior for this class of compounds. The oxidation pathways of a series of substituted anilines in aqueous solution are summarized herein. Cyclic voltammetry, chronopotentiometry, chronoamperometry, and chemical methods were used to identify the reaction products and to elucidate the mechanism of their formation. The compounds studied were aniline, *p*-anisidine, *p*-phenetidine, *p*-chloroaniline, *o*-toluidine, *p*-aminobenzoic acid, *p*-aminobenzonitrile, and *p*-nitroaniline. They were found to undergo a rapid head-to-tail coupling giving the corresponding 4′-substituted 4-aminodiphenylamine in the oxidized form



The most extensive previous investigation of anilines was by Wawzonek and McIntyre who found azobenzenes formed upon oxidation in acetonitrile with pyridine present.[2] Mohilner, *et al.*, whose study was restricted to only aniline in strong acid, identified emeraldine-type final products.[3] Both groups postu-

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[1] Part II: R. F. Nelson and R. N. Adams, *J. Am. Chem. Soc.*, **90**, 3925 (1968).

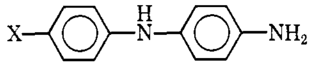
[2] S. Wawzonek and T. W. McIntyre, *J. Electrochem. Soc.*, **114**, 1025 (1967).

[3] D. M. Mohilner, R. N. Adams, and W. J. Argersinger, Jr., *J. Am. Chem. Soc.*, **84**, 3618 (1962).

lated the intermediate formation of 4-aminodiphenylamine in acidic solution, and Wawzonek noted that pH controlled the position of coupling of the cation radicals presumably formed in the initial electrode reaction. The 4-aminodiphenylamine intermediates were also suggested by Daniels and Saunders[4] in the oxidation of anilines with hydrogen peroxide and peroxidase in aqueous media. In the present study, both the 4-aminodiphenylamine (4-ADA) intermediate and the pH control of the products are definitely established.

Experimental Section

A carbon paste electrode of geometric area 0.18 cm^2 was used in sulfuric acid or Britton and Robinson (B & R) buffers. All water was doubly distilled. With the exception of those prepared in this laboratory, all chemicals were purchased from common sources and were purified before use. N,N-Dimethyl-*p*-anisidine was prepared and contributed by Dr. E. T. Seo. The substituted 4-aminodiphenylamines of the structure



were prepared from the 4′-substituted 4-nitrodiphenylamines obtained by the method of Backer and Wadman.[5] Instrumentation for electrochemical and spectrophotometric work was conventional. All potentials mentioned are *vs.* sce and are believed accurate to ±10 mV.

Results

The anilines were first subjected to typical diagnostic electrochemical tests to establish the number of electrons transferred for small-scale electrolysis conditions. These are summarized in Table I. All data were obtained with solution pH = pK_a of each aniline. This was done to equalize the degree of protonation and hence make diffusion coefficient (*D* value) differences as small as possible. Electrode filming was encountered in most cases but reliable results were obtained by working at concentrations from 0.05 to 0.1 m*M*. Rotated disk data ($i_L/\omega^{1/2}C$) are not shown in Table I but were consistent with the other results. The first stage of the oxidation of N,N-dimethyl-*p*-anisidine was used as a model one-electron system to compare and evaluate *n* for the various anilines. The assumption was made that the *D* value of N,N-dimethyl-*p*-anisidine is comparable to that of the various anilines. The first stage of N,N-dimethyl-*p*-anisidine oxidation in water is unequivocally one electron. Details are discussed elsewhere.[6]

Figure 1 shows a cyclic polarogram of *p*-chloroaniline in pH 4.0 buffer run at 8 V/min. It is fairly typical of the polarograms of the other anilines studied here. A single oxidation wave is produced on the first scan which shows no corresponding cathodic current on the reverse sweep. Instead, a new reversible couple is produced at more cathodic potentials. (Figure 1A). In addition, a blue-to-orange solution layer forms on the electrode surface. If controlled-potential electrolyses are carried out on acidic *p*-anisidine or *p*-phenetidine solutions, purple is produced throughout the solution. Upon addition of base, the color changes to yellow. Since the color and acid–base indicator properties resemble those of many molecules having indophenol or indamine structures, compounds of this nature were investigated as the possible follow-up products forming the reversible couple seen in the cyclic polarograms. It soon became evident that this couple corresponds to the 4′-substituted 4-aminodiphenylamine, produced at the electrode in its oxidized form. Identification was usually made by matching cyclic polarograms of the substituted aniline and that of an authentic sample of the suspected follow-up product. A typical identification is seen on Figure 1B which is the cyclic polarogram of an authentic sample of 4-amino-4′-chlorodiphenylamine.

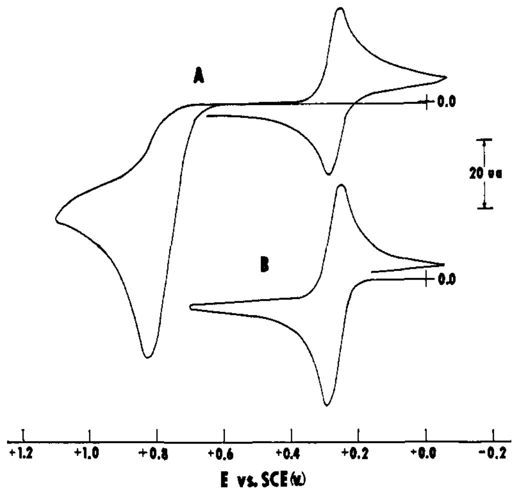


Figure 1. Cyclic polarograms of *p*-chloroaniline and its oxidation product: A, *p*-chloroaniline, pH 4.0; B, 4-amino-4-′chlorodiphenylamine, pH 4.0. Scan starts anodically from 0.0 V.

Table I. Diagnostic Tests for Substituted Aniline Oxidations

Compound	pK_a	$i/V^{1/2}C$[b]	$it^{1/2}/C$[c]	$i\tau^{1/2}/C$[d]	$E_{p/2}$[e]	n[a]
Aniline	4.6	34.6	89.1	116.5	0.72	2
o-Toluidine	4.4	27.1	77.1	109.8	0.67	2
p-Anisidine	5.3	13.4	39.8	48.5	0.44	1
N,N-Dimethyl-*p*-anisidine[f]	5.9	13.2	35.5	56.5	0.40	1
p-Phenetidine	5.3	15.3	36.0	51.9	0.46	1
p-Chloroaniline	4.0	16.9	44.2	61.2	0.73	1
p-Aminobenzoic acid	2.4	28.2	93.4	103.6	0.84	2
p-Cyanoaniline	1.8	29.2	100.6	109.1	1.03	2
p-Nitroaniline	1.0	32.4	101.2	112.0	1.07	2

[a] *n* is the number of electrons transferred; current, *i*, in microamperes; time, *t* or *τ*, in seconds; potential sweep rate, *V*, 7.8 V/min; bulk concentration, *C*, in millimoles/liter. All data taken with solution pH = pK_a listed. [b] Single-sweep peak voltammetry. [c] Chronoamperometry (potentiostatic current–time curves. [d] Chronopotentiometry. [e] Anodic half-peak potential in volts *vs.* sce. [f] Model compound for one-electron comparisons.

Although the cyclic polarogram of Figure 1B matches that of the redox couple seen in Figure 1A such matching should only be taken as supporting, rather than primary evidence for product identification. However, the redox potentials of the substituted 4-ADA'S vary widely with pH and 4′ subtituent. Hence, close matching of the cyclic polarograms over a wide pH range was conceded to provide positive identification in some cases. Spectral and quantitative chemical analysis of controlled-potential electrolyses additionally

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(4) D. G. H. Daniels and B. C. Saunders, *J. Chem. Soc.*, 2112 (1951).

(5) H. J. Backer and S. K. Wadman, *Rec. Trav. Chim.*, 68, 595 (1949).

(6) J. Bacon, R. F. Nelson, and R. N. Adams, to be submitted for publication.

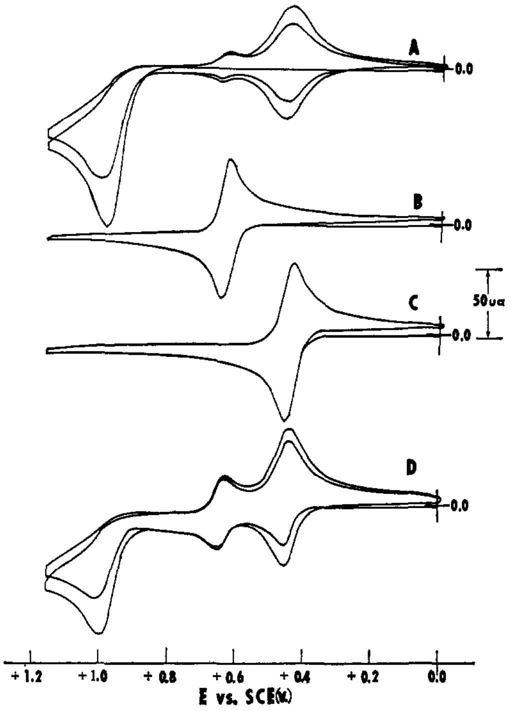


Figure 2. Cyclic polarograms of aniline and its oxidation products: A, aniline alone, pH 2.3; B, benzidine alone, pH 2.3; C, 4-aminodiphenylamine alone, pH 2.3; D, mixture of all three above, pH 2.3. All scans start anodically from 0.0 V.

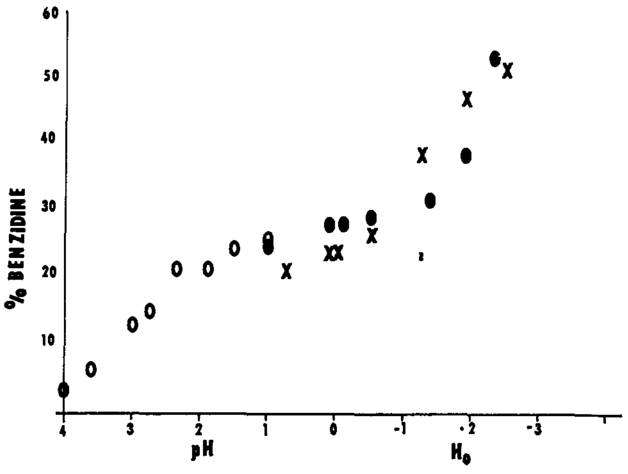


Figure 3. Benzidine formation as a function of acidity: ○, Britton and Robinson buffer; ●, sulfuric acid; ×, perchloric acid. Per cent benzidine determined from ratio of cathodic peaks in cyclic voltammetry.

identified products. These electrolyses were carried out at a platinum gauze electrode with solutions 1 mM in substrate.

In general, then, the initial oxidation of substituted anilines is followed by a fast chemical coupling reaction which produces a 4′-substituted 4-aminodiphenylamine in its oxidized form. The mechanism of formation and details vary and the individual compounds are discussed briefly next.

Aniline. Aniline (and *o*-toluidine) with an unsubstituted *para* position is unique in this series for its follow-up reaction involves both the head-to-tail coupling to give the 4-ADA derivative and tail-to-tail coupling to give an oxidized benzidine.

The anodic wave for aniline corresponds to two electrons per molecule. Two follow-up couples were seen which were identified as benzidine and 4-aminodiphenylamine. Figure 2 shows cyclic polarograms of (A) aniline alone at pH 2.3, (B) benzidine, (C) 4-aminodiphenylamine, and (D) a mixture of all three. This is an exceptionally good example of matching of cyclic polarograms and leaves practically no doubt as to product identity.

The amount of benzidine formed was quite pH dependent. Figure 3 shows that the amount of benzidine increases with acidity. Above pH 4 only a trace of benzidine is seen in the cyclic polarograms. Relative amounts of benzidine *vs.* 4-ADA were determined by reverse-current chronopotentiometry and cyclic voltammetry. In the latter case, the potential was held about 50 mV past the aniline anodic peak for 15 sec, then scanned cathodic at 8 V/min. Thus, the time of the cathodic scan was small compared to the time of product generation. The measurements are necessarily semiquantitative since the closeness of the reduction peaks for the two compounds made it necessary to estimate the base of the 4-aminodiphenylamine peak. The accuracy of both methods is around ±10%. Nevertheless, the trend is quite definite.

Using reversal chronopotentiometry (i_r/i_f = 0.414), the total reverse transition time is 0.4 times the forward transition time. This indicates all of the oxidized aniline is accounted for by the coupled products. There were no indications of the *ortho* coupling product, 2-aminodiphenylamine.

The previous aniline oxidation in strong acid by Mohilner, Argersinger, and Adams did not employ cyclic voltammetry and benzidine intermediates were not detected. In light of the present results it is unlikely that the emeraldine-type octamer is made up entirely of head-to-tail coupled units.

***o*-Toluidine.** The behavior of the *o*-toluidine is suspected to parallel that of aniline in almost every respect. The potentials of the follow-up couples differ only slightly from those of benzidine and 4-ADA, and the product ratios have the same pH dependence. However, because the 2′,3-dimethyl-4-aminodiphenylamine and the 3,3′-dimethylbenzidine are not available and their preparations are tedious, absolute identification of these products has not been made. We feel certain, however, that once the compounds are prepared they can be shown to be the follow-up products.

***p*-Chloroaniline.** The main oxidation peak of *p*-chloroaniline corresponds to one electron per molecule. The cyclic voltammogram is shown in Figure 1. Reverse chronopotentiometry shows that all the *p*-chloroaniline oxidized is accounted for by the reverse transition time corresponding to the 4-amino-4′-chlorodiphenylamine. Controlled-potential electrolysis of the aniline at a platinum gauze electrode at pH 3.1 yields one electron per molecule and an orange solution. In a typical electrolysis, 0.0583 mmol of *p*-chloroaniline was exhaustively electrolyzed at pH 3.1. The resulting solution was analyzed for chloride ion by potentiometric titration with standard silver nitrate. The titration results indicated 0.0296 mmol of chloride present. Since 2 mol of *p*-chloroaniline produces 1 mol of ejected chloride ion in the coupling reaction, this corresponds to a chloride recovery of about 101%. Furthermore, the optical spectrum of the solution from a controlled potential electrolysis of *p*-chloroaniline matched that of an electrochemically oxidized solution of authentic 4-amino-4′-chlorodiphenylamine. At pH 3.5 the optical spectra of both solutions showed two broad peaks with maxima at 294 and 475 $m\mu$.

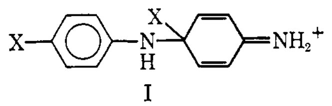
p-**Anisidine and** *p*-**Phenetidine.** Both of these compounds head-to-tail couple in an over-all one-electron step, presumably ejecting methoxide and ethoxide ion, respectively. The optical spectra of solutions from controlled-potential electrolyses are identical with those from oxidation of authentic samples of the corresponding 4′-substituted 4-ADA'S. At pH 3.5 absorption maxima appear at 332 and 540 $m\mu$ with practically no differences between the methoxy and ethoxy derivatives. However, the cyclic voltammetry of both compounds shows the presence of a small amount (*ca.* 10%) of an additional redox couple at potentials about 250 mV cathodic of the diphenylamine system. This as yet has not been identified. Reverse-current chronopotentiometry showed that all the oxidized starting material was accounted for by the two systems.

p-**Aminobenzoic Acid.** Electrochemical studies of this compound were complicated by electrode filming except at low concentrations. Still, in 1 m*M* solutions good identification was made of 4-amino-4′-carboxydiphenylamine as the product of the oxidation. Reverse-current chronopotentiometry confirmed an over-all two-electron process and showed that the 4-ADA is the only follow-up product. Because of filming, no complete electrolysis was attempted. The *p*-sulfo derivative, sulfanilic acid, appears to behave similarly.

p-**Cyanoaniline and** *p*-**Nitroaniline.** The cyclic voltammograms of these compounds are very poorly defined. Although there are clear indications that the corresponding substituted diphenylamines are formed by head-to-tail coupling, definite product identification has not been possible. Further chemical and electrode reactions are evidently present with these systems.

Discussion

The results show the major products of anodic aniline oxidations in aqueous solution are the head-to-tail coupled dimers, the 4′-substituted 4-aminodiphenylamines in their oxidized forms. As was suggested by Daniels and Saunders,[4] these products proceed logically from an intermediate (I).

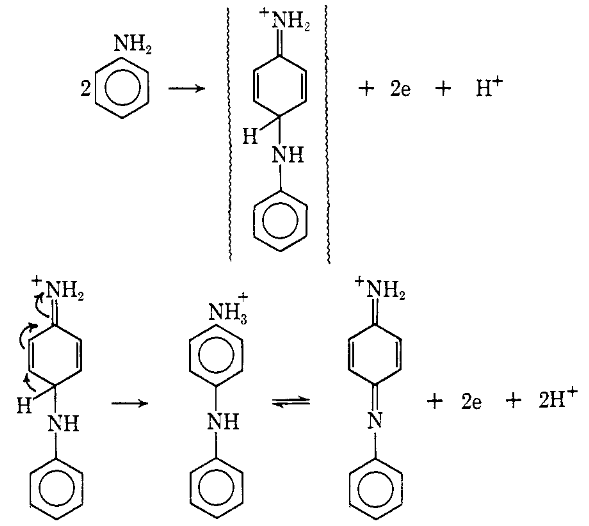


I

If the central X leaves as an anion, then the over-all electrochemical reaction should correspond to a one-electron process (two electrons total per two molecules of substituted aniline). This is unequivocally proven for the case of *p*-chloroaniline. Both the voltammetry and the quantitative chloride analysis in controlled-potential coulometry correspond precisely to this stoichiometry. The major pathway for *p*-anisidine and *p*-phenetidine follows this one-electron pattern presumably with ejection of methoxide and ethoxide ion, respectively.

On the other hand, if the electron pair of the X remains with intermediate (I) (*i.e.*, if X leaves as a cation or in an oxidized form), then the 4-aminodiphenylamine is formed in a reduced state and the over-all process follows an ece mechanism (electron transfer–chemical reaction–electron transfer). The sequence is shown for aniline in Scheme I. A total of four electrons per two molecules of aniline produces an over-all two-electron net process. This reaction is common to aniline, *o*-toluidine, and *p*-aminobenzoic acid. In the latter case CO$_2$ is presumably the leaving group. In addition, aniline and *o*-toluidine with unsubstituted *para* positions split their coupling reactions between head-to-tail and tail-to-tail (benzidine) formation. A quantitative interpretation of the 4′-aminodiphenylamine to benzidine ratios as a function of acidity requires further study.

Scheme I



The question as to the mode of formation of the intermediate (I) remains. Both the peroxidase studies and previous electrochemical work have favored a coupling of two aniline cation radicals.[2-4] In addition, Goldschmidt and Wurzschmitt successfully trapped the radical produced *via* peroxide oxidation of aniline using triphenylmethyl radical and isolated the product.[7]

However, an ionic mechanism involving an initial two-electron oxidation of one molecule of aniline followed by nucleophilic attack of parent will produce the same intermediate (I), and the same stoichiometry and reaction path. It must be emphasized that the coupling reactions are rapid enough that no reverse current results from the main oxidation using any electrochemical techniques available to us. Therefore, while the existing evidence from chemical oxidations favors the radical ion coupling, this point remains ambiguous.

Acknowledgment. The support of this work by the National Science Foundation *via* Grant GP-5079X is gratefully acknowledged.

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(7) S. Goldschmidt and B. Wurzschmitt, *Ber.*, **55**, 3216 (1922).