ammonia (4)–(5). The maximum half-life of 10^{-2} sec. which we have estimated[22] for the exchange is in agreement with the high rates estimated[27] for other comparable protolytic reactions. Our finding that reaction 2 decelerates so much is not unexpected; it has been known for some time that alkoxide ion slows the rate of the reaction of an alcohol with alkali metal. However, our quantitative evaluation of this deceleration, and its mechanistic interpretation, are new, and perhaps useful.

In effect our conclusion for hydrogen liberation from an electron–alcohol–ammonia system is as follows. When there is no base stronger than the solvent present, the alcohol produces ammonium ions (which are immediately reduced by electrons) more rapidly than electrons directly reduce the alcohol (or its ion pair). Strong base (e.g., alkoxide produced in the reaction) so complexes (proton bonds) the alcohol that its production of ammonium ions is sufficiently slow to allow direct reduction of the complex by electrons.

The quantitative effect of alkoxide on hydrogen liberation may be calculated with equations 11 and 13. For example, one interesting comparison is the time which would be required for 20% reaction of 0.1 M sodium with 0.1 M ethanol; first, initially

in pure ammonia and, second, initially with 0.1 M ethoxide ion in the ammonia. Reaction of 20% of the alcohol would, in the first experiment, require less than one minute; in the second, over 3 hr. In other words, addition of an equimolar amount of ethoxide ion to the ethanol would, in this experiment, increase the time for 20% reaction by a factor of about 200. Such knowledge as this might be of use in the reduction of other compounds by sodium and alcohol in ammonia, where it is desirable to avoid competition by reaction 2.[3c]

Certainly competition by reaction 2 should be considered in the kinetic evaluation of any reactions of the alkali metals with other compounds in the presence of alcohol.[28] Also, our finding of a change in kinetic order after the initial 25% of reaction is of interest in connection with any "initial-rate" kinetic studies[29] which may involve alcohols and metals in ammonia.

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Investigation of the Kinetics and Mechanism of the Anodic Oxidation of Aniline in Aqueous Sulfuric Acid Solution at a Platinum Electrode[1,2]

BY DAVID M. MOHILNER,[3] RALPH N. ADAMS AND WILLIAM J. ARGERSINGER, JR.

It is proposed that the anodic oxidation of aniline in aqueous sulfuric acid solution at a platinum electrode proceeds through a free radical mechanism and that the final product of this electrode reaction is primarily the octamer emeraldine, or a very similar compound. This mechanism is based upon measurement of kinetic parameters for the initial charge transfer step and upon direct comparison of the properties, including the infrared spectrum, of the precipitate formed on the anode and those of chemically synthesized compounds.

Introduction

Nearly a century ago, Letheby[4] discovered that the final product of the anodic oxidation of aniline in aqueous sulfuric acid solution at a platinum electrode is a dark green precipitate. Subsequent investigators[5–7] verified this result and called the precipitate "aniline black." Similar results were also reported[8,9] for hydrochloric acid solutions of aniline. In 1935, a reaction scheme for the anodic oxidation of aniline at a carbon electrode was

suggested.[10] No further research on this electrode reaction was carried out until the last decade when Khomutov and Gorbachev re-examined it.[11–15] They again verified Letheby's original observation about the green precipitate. In addition, on the basis of current–time curves, two different mechanisms for the electrode reaction were proposed.

In the present paper, evidence is presented for a mechanism which is quite different from either of those of Khomutov and Gorbachev. It is based upon a characterization of the chemical nature of the final product of the anodic oxidation of aniline and upon an analysis of polarization curves.

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(2) Taken in part from the dissertation of David M. Mohilner submitted to the Department of Chemistry and the Faculty of the Graduate School of the University of Kansas in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) Department of Chemistry, Louisiana State University, Baton Rouge, La.

(4) H. Letheby, *J. Chem. Soc.*, **15**, 161 (1862).

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(6) M. A. Rosenstiehl, *ibid.*, **81**, 1275 (1875); *Ann. Chim. Phys.*, [5] **8**, 561 (1876).

(7) F. Goppelsroeder, *Compt. rend.*, **82**, 331, 1392 (1876).

(8) L. Gilchrist, *J. Phys. Chem.*, **8**, 539 (1904).

(9) J. W. Shipley and M. T. Rogers, *Can. J. Res.*, **B17**, 147 (1939).

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(12) N. E. Khomutov and S. V. Gorbachev, *Soveshch. Elektrokhim.*, 1950, *Izdat. Akad. Nauk SSSR*, Moscow, 1953, pp. 579–585.

(13) N. E. Khomutov, *Zhur. Fiz. Khim.*, **25**, 607 (1951).

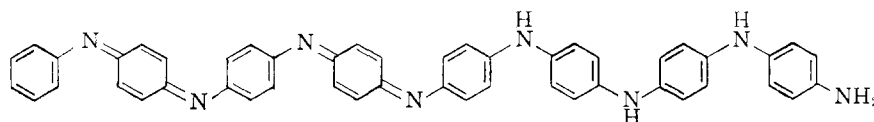(14) N. E. Khomutov, *J. Gen. Chem. USSR*, **22**, 627 (1952).

(15) N. E. Khomutov, Reports of the Fourth Soviet Conference on Electrochemistry, Oct. 1–6, 1956, Consultants Bureau Inc., New York, N. Y., 1958.
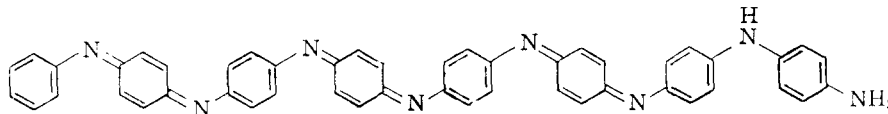
Nature of the Final Product

The descriptions of the anode precipitate given in the literature reveal that it is a stable, dark green, amorphous substance, not melting up to 300°. It is insoluble in water, solutions of mineral acids and bases, and most of the common organic solvents. It changes to violet-blue in color on immersion in dilute ammonia water. It dissolves in concentrated sulfuric acid with a purplish-brown color, but, when the solution is diluted, a green precipitate forms once more. Although the early workers called it "aniline black" it is clear that these properties bear little resemblance to those of the so-called "ungreenable" aniline black of commerce. However, these properties are strikingly similar to those of one of the intermediates of aniline black, emeraldine.

This compound is the parent member of a group of five intermediates of aniline black, known as the emeraldine series. They were discovered by Green[16-18] and his co-workers early in this century.

Emeraldine has the formula

aniline in sulfuric acid using a platinum anode. The aniline concentration was 0.01 M; sulfuric acid was 1 M, and the anode potential was maintained at +0.8 v. vs. S. C. E.

The synthesized samples of emeraldine and nigraniline behaved as reported by Green. In addition, both substances were amorphous and neither melted up to 300°. The specimen of the anode precipitate exhibited the properties reported previously in the literature. In addition, it was found that the basic form dissolved in cold 80% acetic acid with the same green color as emeraldine. The pyridine and N,N-dimethylformamide solutions had the same bright blue color as emeraldine and nigraniline. For further comparison, infrared spectra of the three substances were obtained by the KBr pellet method using a Perkin-Elmer model 21 infrared spectrophotometer.

In each spectrum there are five major absorption peaks. In the case of emeraldine these occur at approximately 1595, 1500, 1300, 1170 and 830 cm.$^{-1}$. For nigraniline the peaks occur at approximately 1590, 1502, 1305, 1150 and 830 cm.$^{-1}$. The emeraldine spectrum shows a break at 1150 cm.$^{-1}$ while the nigraniline spectrum has a break at 1170 cm.$^{-1}$. In the case of the anode precipitate the peaks occur at approximately 1587, 1502, 1297, 1145 and 830 cm.$^{-1}$. A minor peak occurs on this spectrum at 1450 cm.$^{-1}$. The spectra of emeraldine and nigraniline both have incipient peaks at this frequency. All three spectra have a minor peak at 1380 cm.$^{-1}$, a shoulder in the neighborhood of 1230 cm.$^{-1}$ and another shoulder around 1120 cm.$^{-1}$.

It is a violet-blue base forming dark green salts. Like the anode precipitate it is insoluble in most common solvents, but it does dissolve in concentrated sulfuric acid yielding a purplish-brown solution. On dilution with water this solution gives a dark green precipitate of emeraldine sulfate. Emeraldine will not dissolve in glacial acetic acid; it will, however, form a green solution in cold 80% acetic acid. It dissolves in cold pyridine or N,N-dimethylformamide with the production of a bright blue color. The salts of emeraldine are quite stable. The base may be oxidized in ammoniacal media to nigraniline

The infrared spectra indicate that the anode precipitate is structurally similar to both emeraldine and nigraniline (perhaps slightly more like nigraniline). The fact that the spectrum of the anode precipitate is not identical in every detail with either of the chemically synthesized compounds may imply that the electrochemically produced material is not a single substance but, rather, a mixture of nigraniline and emeraldine. The marked similarities in the other properties of the anode precipitate and emeraldine, in particular of the solutions in 80% acetic acid, argue strongly

This is a dark blue base, forming blue salts. Its solubility properties are similar to those of emeraldine. The solution in cold 80% acetic acid is blue in contrast to emeraldine. The pyridine and N,N-dimethylformamide solutions of nigraniline are bright blue and are difficult to distinguish from the corresponding solutions of emeraldine. Nigraniline dissolves in concentrated sulfuric acid yielding a violet color, but, on dilution, a green precipitate of emeraldine sulfate is formed. The nigraniline base is stable; the salts are very unstable.

Experimental

The emeraldine and nigraniline were prepared according to the directions of Green.[18] The anode precipitate was prepared by constant potential electrolysis of a solution of

for the hypothesis that the anodically formed material is *principally* emeraldine.

Electrochemical Kinetics

Preliminary studies of the anodic oxidation of aniline in stirred sulfuric acid solution at a platinum anode indicated that a plot of the logarithm of the current as a function of the anode potential obeyed Tafel's law. It was, therefore, decided to carry out a systematic investigation of the polarization curves in stirred solution by the method of controlled potential scanning. For this purpose, an instrument using operational amplifiers which was a modification of a circuit originally designed by Booman[19] was constructed.[20] With this instrument controlled potential polarization curves could be automatically recorded. Its advantage

(16) A. G. Green and A. E. Woodhead, *J. Chem. Soc.*, **97**, 2388 (1910); **101**, 1117 (1912).

(17) A. G. Green and S. Wolff, *Ber.*, **46**, 33 (1913).

(18) A. G. Green and W. Johnson, *ibid.*, **46**, 3769 (1913).

(19) G. L. Booman, *Anal. Chem.*, **29**, 213 (1957).

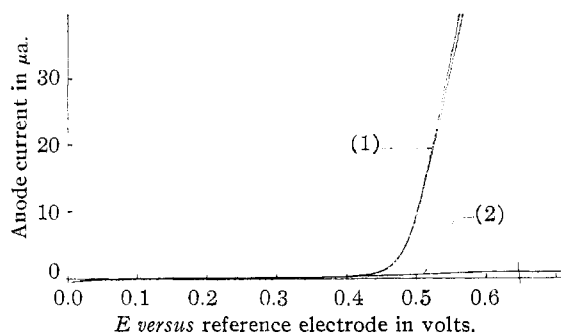(20) D. M. Mohilner, Dissertation, University of Kansas, 1961.

Fig. 1.—Typical set of polarization curves: (1), aniline 0.01132 M in 3.72 m H_2SO_4 at 19.9°; (2), 3.72 m H_2SO_4 at 19.9°.
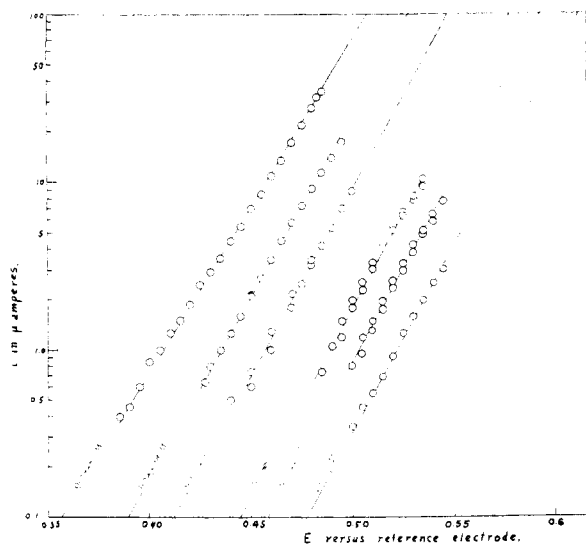

Fig. 2.—Tafel lines for anodic oxidation of aniline in 3.72 m H_2SO_4 at 19.9°; aniline concentrations, left to right, 0.04260 M, 0.02208 M, 0.01132 M, 0.00426 M, 0.00221 M, 0.00113 M.

over the ordinary polarographic method lies in the fact that no correction is required for the voltage drop through the solution.

Two series of polarization experiments were carried out; in the first the temperature was held constant and the aniline concentration was varied, and in the second the aniline concentration was held constant and the temperature was varied.

Experimental.—Technical grade aniline was distilled four times over zinc dust. The refractive index for the sodium D line of the product of the fourth distillation, measured with a Bausch and Lomb refractometer at 34.9°, was 1.577. The refractive index at this temperature calculated from the data for pure aniline[21] is 1.578.

The distilled water used in preparing the solutions was passed through a mixed cation–anion exchange resin in a Crystalab Deminizer. The ionic impurity level of the product was less than 0.2 p.p.m.

All other chemicals were reagent grade and were used without further purification.

The background electrolyte used in all of the polarization experiments was an aqueous solution of sulfuric acid whose concentration was 3.72 molal. Six solutions of aniline in this background electrolyte were prepared. Their concentrations were 0.00113, 0.00221, 0.00426, 0.01132, 0.02208
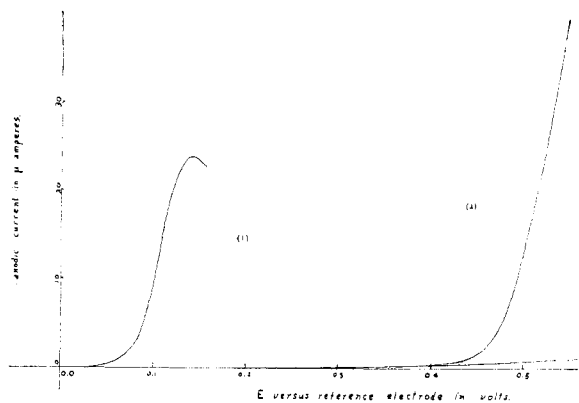

Fig. 3.—Comparison of the electrochemical behavior of p-aminodiphenylamine and of aniline at 25° in 3.72 m H_2SO_4: (1), 0.001 M p-aminodiphenylamine; (2), 0.01132 M aniline.
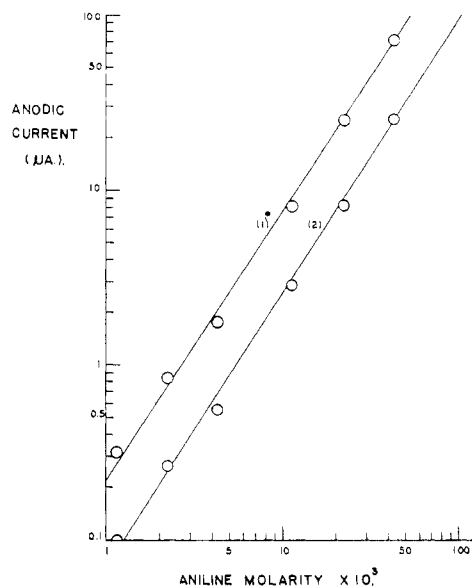

Fig. 4.—Variation of the logarithm of the current with the logarithm of the concentration of aniline at constant anode potential and temperature; temperature, 19.9°: (1), E = 0.500 v.; (2), E = 0.478 v.

and 0.04260 molar. These solutions were stored in the dark.

In an effort to minimize the effects of mechanical working on the surface of the anode, an electro-polished platinum microelectrode was used. It was made from a platinum wire of high purity. One end of this wire was threaded and screwed into the end of a brass rod which served as a handle to avoid having to touch the wire and also provided electrical contact during electropolishing and later in polarization experiments. The electropolishing bath was a fused eutectic mixture of $KCl-NaCl$.[22] It was contained in a platinum crucible mounted on a clay triangle over a bunsen burner. The crucible served as cathode in the electropolishing cell. After electropolishing, the platinum wire was sealed into a soft glass tube.

Before each controlled potential scan this electrode was cleaned in chromic acid and then cathodically reduced to remove platinum oxide.

In order to minimize the liquid junction potential and to eliminate any possible extraneous effects of chloride ion from an S.C.E. a mercury–mercurous sulfate–sulfuric acid reference electrode was used.[23] The concentration of

(21) "International Critical Tables," Vol. VII, Maple Press Co., York, Pa., 1930, p. 12.

(22) P. R. Rowland, *Nature*, **171**, 931 (1953).

(23) H. S. Harned and W. J. Hamer, *J. Am. Chem. Soc.*, **57**, 27 (1935).

sulfuric acid used in the reference electrode was the same as that of the background electrolyte. The reference electrode was connected to the cell through a Haber–Luggin capillary.

The cathode (auxiliary electrode) was a platinum foil.

Polarization experiments were carried out in a constant temperature water-bath. The experiments at constant temperature and varying aniline concentration were carried out at 19.9°, while those at constant aniline concentration (0.01132 molar) were carried out at 0.1, 19.9, 25.2, 30.4 and 35.7°.

The solutions were magnetically stirred using a Teflon covered stirring bar. This bar was driven by a rotating magnet mounted on Teflon bearings under water inside the constant temperature bath and driven externally by a pulley arrangement. Preliminary experiments determined a stirring rate which was fast enough that further increase in speed produced no change in the initial portions of the polarization curves. Under these conditions mass transfer control was essentially eliminated.

Test solutions were deaerated by nitrogen bubbling prior to the recording of polarization curves. The nitrogen was first passed over hot copper in an electric furnace to remove traces of oxygen and was then bubbled through a sample of background electrolyte.

A typical set of polarization curves as actually recorded is shown in Fig. 1.

Results.—A graph of the logarithm of the net current[24] for the anodic oxidation of aniline as a function of the anode potential was prepared from the set of polarization curves corresponding to each of the experimental conditions mentioned above. A typical set of these Tafel lines for varying aniline concentrations is shown in Fig. 2.

In view of the fact that the final product in this electrode process is emeraldine or a similar compound it is clear that this electrode reaction must involve a sequence of charge transfer steps. Hence, it is necessary to have an idea which of these charge transfer steps is rate controlling in order to interpret the slopes of the experimentally obtained Tafel lines.

A likely intermediate in the oxidation of aniline to emeraldine is p-aminodiphenylamine. Furthermore, emeraldine may be synthesized from this compound under the same conditions that it can be synthesized from aniline. It was therefore of interest to compare the electrochemical behavior of these two compounds. It was found that the electrochemical oxidation of p-aminodiphenylamine gave rise to a dark green precipitate which was qualitatively similar to emeraldine. Moreover, p-aminodiphenylamine was electrochemically oxidized much more easily than aniline. This is shown in Fig. 3 in which the polarization curve on the left corresponds to 0.001 M p-aminodiphenylamine while that on the right corresponds to 0.01 M aniline. Thus, if p-aminodiphenylamine is one of the intermediates in the electrochemical oxidation of aniline to emeraldine, then all of the succeeding intermediates are also much more easily oxidized than aniline. This implies that in the electrochemical oxidation of aniline to emeraldine the first charge transfer step should be rate controlling. On this assumption it may be shown that the slope of a Tafel line for the anodic oxidation of aniline will be $\alpha n_a F/2.303 RT$, where α is the transfer coefficient and n_a is the number of electrons involved in the initial charge transfer step; R, T and F have their usual significance. The slope of each Tafel line was computed. In every

case the value of the product αn_a was in the neighborhood of 1.2 to 1.3. Since the transfer coefficient must be less than unity it follows that n_a, which is an integer, must be greater than unity. The value of the transfer coefficient was calculated on the assumption that $n_a = 2$. The average value for the anodic transfer coefficient, α, was 0.65 ± 0.01 at the 95% confidence level.

From the Tafel lines obtained at constant temperature with varying aniline concentration the logarithm of the current was plotted against the logarithm of the corresponding aniline concentration. Two such graphs are shown in Fig. 4. Their slopes are 1.6 to 1.7. According to theory the slope of such lines should be equal to the number of aniline molecules involved in the initial charge transfer step. These data were interpreted as meaning that the initial charge transfer step is second order with respect to aniline since the slopes always were closer to 2 than to 1. It is possible that specific adsorption may account for the non-integral order found.

Only two initial products from the first charge transfer reaction seem at all likely. These are the dipositive ion (2 electron removal) or the free radical cation (1 electron transfer). Energetically the latter is probably more feasible and offers greater possibilities of resonance stabilization. With $n_a = 2$ and the reaction second order with respect to aniline, the radical ion is the indicated intermediate. This is in marked contrast to the anodic oxidation of N,N-dimethylaniline[25] and N-methylaniline,[26] where 2 electrons are transferred in the rate step with the reaction order unity, leading to the dipositive ion intermediate. That this whole pattern is coherent is evidenced by the fact that N-methyl- and N,N-dimethylaniline lead to N-methylated benzidines (tail-to-tail coupling) upon anodic oxidation, whereas aniline gives condensation products with –NH– linkages (head-to-tail).

From the Tafel lines obtained at constant aniline concentration with varying temperature, the logarithm of the ratio of the current divided by the absolute temperature was plotted against the reciprocal of the absolute temperature at various (constant) values of the anode potential. These plots were linear and their slopes gave a value for the apparent standard enthalpy of activation of 29.2 ± 0.1 kcal./equivalent.

On the basis of the foregoing experimental evidence it is suggested that the anodic oxidation of aniline under the conditions mentioned proceeds according to the scheme

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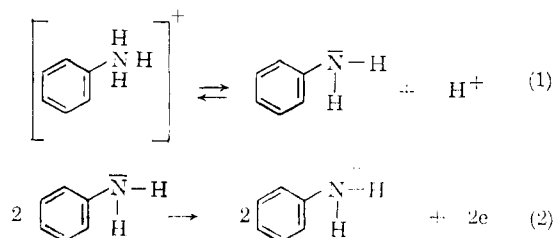
(24) The net current was determined by taking the difference between the current on the aniline polarization curve and on the background polarization curve at the same value of E.

(25) Z. Galus and R. N. Adams, *J. Am. Chem. Soc.*, **84**, 2061 (1962).

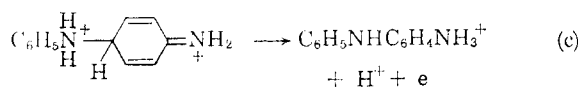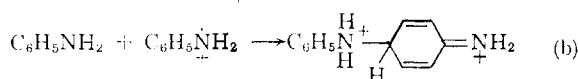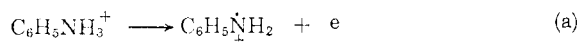(26) Z. Galus and R. N. Adams, Abstracts, 140th A.C.S. Meeting, Chicago, Ill.
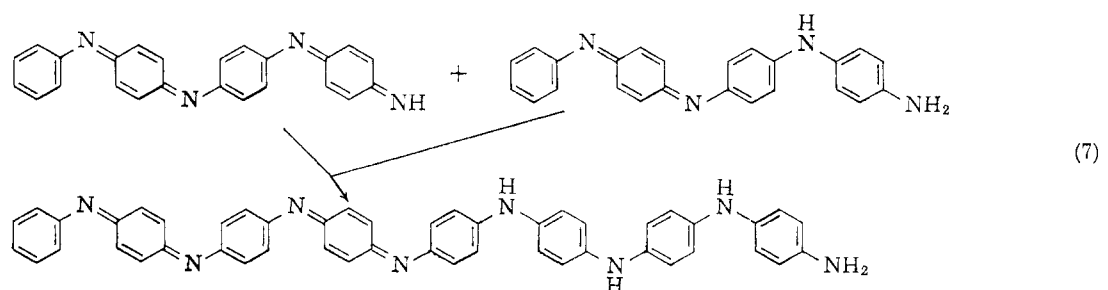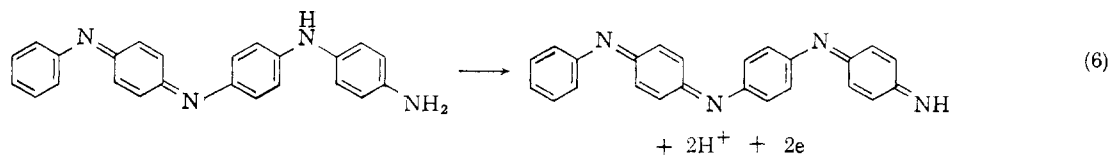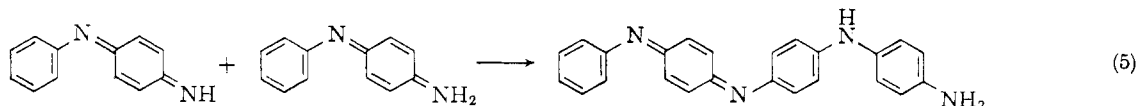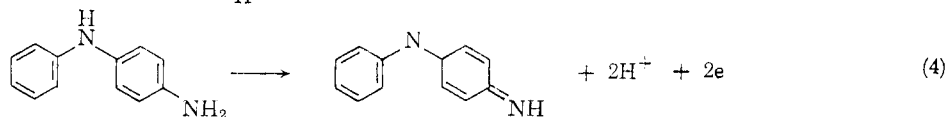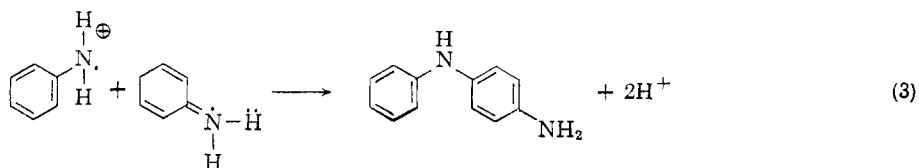
Reaction 2 is the initial charge transfer step and is rate controlling in accordance with the kinetic data obtained. Nothing is known about the succeeding steps in the reaction except that they must be fast. The sequence of reactions actually written down (steps 4–7) is the same as that given by Green[17] for the chemical oxidation path from aniline to emeraldine. It is possible that those charge transfer steps which are shown as two electron steps, reactions 4 and 6, may also proceed through free radical mechanisms.[26]