NOTES

A Polarographic Examination of Diazotized Amines. II. Additional Coulometric Data

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Our interpretation of the polarographic behavior of benzenediazonium salts[2] was aided by coulometric analyses carried out at pH 7. This study has been extended to include data obtained at pH 4.1 and pH 1.1 with benzenediazonium chloride and at pH 7 with o-carboxybenzenediazonium chloride. We have observed that in the pH range studied there is no change in the electron consumption at a particular potential, as was indicated earlier by the small change in i_d/C for the total second wave.

We have continued to observe that the electron consumption at -0.6 v. $vs.$ S.C.E. was 1 electron/ mole RN_2X, but in contrast to our earlier observation we now find that the electron consumption at -1.2 v. $vs.$ S.C.E. is 2 electrons/mole RN_2X. This new value has been observed not only at the pH values studied for the first time in our present work but also at pH 7 used previously.

In seeking an explanation for this serious discrepancy at the more negative potential we discovered that when a typical coulometric analysis of millimolar benzenediazonium chloride was interrupted after but 1 electron/mole RN_2X was consumed the solution in the cell had no polarographic activity. It was this criterion which led us to conclude in our earlier work that the electrolysis was complete.[3] This criterion was false, for when the solution was removed from the cell and allowed to stand in the cold polarographic activity returned slowly. This same phenomenon was observed with partially electrolyzed solutions at -0.6 v. also. This return of polarographic activity was not noted after the consumption of 1 electron/mole RN_2X at -0.6 v. or of 2 electrons/mole RN_2X at -1.2 v. The complete disappearance of polarographic activity from partially electrolyzed solutions of diazotized anthranilic acid was not observed and the electron consumption at the more negative potential was 2 electrons/mole RN_2X.

It is apparent that in the case of diazotized aniline the solution must contain a reservoir of material in equilibrium with the substances responsible for the two polarographic waves but not itself reducible at the potentials available to us. Our interpretation of the polarographic results[2] ascribed the second wave to the undissociated diazohydroxide. It is reasonable to continue to apply the classical hypothesis and ascribe the second wave to the syn-diazohydroxide while the

reservoir substance becomes the less reactive $anti$-diazohydroxide. Our results demonstrate that such a reservoir substance is not an important part of diazotized anthranilic acid.

Throughout our current work we have continued to observe the mobile equilibrium between the substances responsible for the first and second polarographic waves; these waves invariably appear with diffusion currents in the same proportion and diffusion currents decrease according to the Ilkovic equation as drop times are increased from 2.6 to 4.5 seconds.

Since we now know that 2 electrons/mole RN_2X are involved in the second polarographic wave our original equation (C)[2] becomes (C').

(C) $R—N=N—OH + H^+ + e \longrightarrow R\cdot + N_2 + H_2O$

(C') $R—N=N—OH + 2H^+ + 2e \longrightarrow$
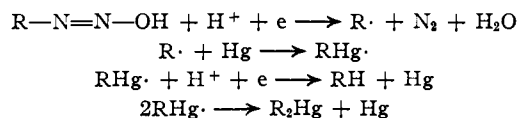$$2RH + N_2 + H_2O$$
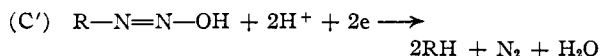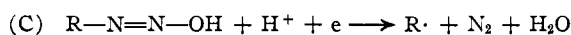
Alternate expressions for (C') to indicate a free radical intermediate may be written; disintegration of the mercury cathode and the formation of tarry products was observed in coulometric work at the more negative potential as well as at -0.6 v. where a 1 electron process occurs.[4]

Our coulometric work does not support the assertion of Elofson, Edsberg and Mecherly[5] that a four electron process leading to the hydrazine is responsible for the total polarographic activity of diazo compounds.[6] Our earlier work has shown that the second wave represents the reduction of a substance entirely different from that responsible for the first wave but in equilibrium with it.

Since it is unlikely that we shall be able to continue our work in this field we wish to take this opportunity to call attention to the work of Rheaume[7] who carried out a detailed study of the polarographic behavior of diazotized aniline in the range $+0.1$ to -0.1 v. $vs.$ S.C.E. At high galvanometer sensitivities it was possible to detect a small wave which occurred just prior to the first major wave. The diffusion current of this small wave was proportional to concentration in the case of the chloride salt and much smaller and not proportional to concentration in the case of the bisulfate salt. Many hypotheses were examined experimentally but no conclusions were reached.

(1) Dewey and Almy Chemical Co., Cambridge 40, Mass.

(2) E. R. Atkinson, H. H. Warren, P. I. Abell and R. E. Wing, This Journal, 72, 915 (1950).

(3) A less satisfactory criterion was a decrease in the current flowing through the cell to the pre-electrolysis value of 1 ma. or less. This appears to have been because of poor stirring.

(4) A sequence suggested by the referee is

$R—N=N—OH + H^+ + e \longrightarrow R\cdot + N_2 + H_2O$
$R\cdot + Hg \longrightarrow RHg\cdot$
$RHg\cdot + H^+ + e \longrightarrow RH + Hg$
$2RHg\cdot \longrightarrow R_2Hg + Hg$

(5) R. M. Elofson, R. L. Edsberg and P. A. Mecherly, J. Electrochem. Soc., 97, 166 (1950).

(6) S. Wawzonek (Anal. Chem., 24, 36 (1952)) accepts the four electron process of the above authors and believes that our observed electron consumption of 1 (now 2) electrons/mole RN_2X can be attributed to the stirring in the coulometric cell which sweeps away the initial reduction products before all four electrons are absorbed.

(7) L. A. Rheaume, B.S. Thesis, University of New Hampshire, 1950.

This small wave was not observed in the case of other diazo compounds studied in this Laboratory.

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Experimental

o-Carboxybenzenediazonium chloride was prepared from anthranilic acid by a method similar to that used for benzenediazonium chloride.[2] Other materials and apparatus were the same as those used earlier.[2] Our coulometric cell had a capacity about twice that of the original model and this required very careful deaeration to avoid interference from hydrogen peroxide waves which were encountered at pH 4.1 and pH 1.1. At these pH values (in contrast to pH 7 where it was negligible) the non-electrolytic decomposition of diazotized aniline in the presence of the large stirred mercury cathode became noticeable. The extent of decomposition during the 40–90 min. required for a typical coulometric analysis was measured by noting the decrease in the diffusion currents of either wave. It was observed that, for example, the actual electron consumption at -0.6 v. (0.90 electron/mole RN_2X) was raised to the integral value by correction for the non-electrolytic decomposition. In cases where the electrolysis was interrupted at an intermediate stage it was necessary to remove the solution from contact with the cathode since the non-electrolytic decomposition of the diazo compound was still more rapid in the presence of the mercury dust which accumulated on the cathode during electrolysis. It was only our good fortune in removing a partially electrolyzed solution from the cell which permitted us to observe the increase in polarographic activity which occurred on standing. The increase in diffusion currents was observed by recording polarograms of fresh portions of the solution at 15-minute intervals. It was observed that the return of polarographic activity continued for about one hour.

No difficulty from non-electrolytic decomposition was experienced with diazotized anthranilic acid.

Coulometric analyses performed during the present work showed a precision of 2%.

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Acrylates of Difficultly Esterified Alcohols

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The use of trifluoroacetic acid anhydride as an esterification agent has been extended to the preparation of acrylate esters of alcohols which normally need to be treated with acrylyl chloride or acrylic anhydride.

The procedure is essentially that of Bourne, Stacey, Tatlow and Tedder[1] who used trifluoroacetic acid anhydride in the esterification of alcohols and phenols. In this process, the alcohol is added to a mixture of acrylic acid and trifluoroacetic acid anhydride. The resulting acrylate ester is easily recovered in very good yield by washing and distilling.

This procedure was developed primarily for the production of acrylate and methacrylate esters of 1,1-dihydroperfluoroalkyl alcohols, but it also worked very well when applied to the preparation of phenyl acrylate. As noted by previous workers[1,2] the only ester formed is the one resulting from esterification with the non-fluorinated carboxylic acid.

(1) E. J. Bourne, M. Stacey, J. C. Tatlow and J. M. Tedder, J. Chem. Soc., 2976 (1949).
(2) P. W. Morgan, THIS JOURNAL, 73, 860 (1951).

Experimental

Preparation of Phenyl Acrylate.—To a 2-liter 3-necked flask immersed in an ice-bath and equipped with reflux condenser, stirrer, dropping funnel and thermometer is added 288 g. (4 moles) of hydroquinone inhibited glacial acrylic acid. Trifluoroacetic acid anhydride (840 g., 4 moles) is then added through the dropping funnel at such a rate that the temperature of the stirred solution does not exceed 15°. Stirring is continued 15 minutes after the addition of the anhydride and during the addition of the phenol (376 g., 4 moles), which is added at such a rate that the temperature of the cooled mixture does not exceed 25°. After 90 minutes additional stirring, the reaction mixture is transferred to a separatory funnel and water is added until two layers separate. The top ester layer is washed with water, 5% NaOH and again with water. Using hydroquinone and copper flake as inhibitors, two distillations through an efficient column packed with glass helices produced 332 g. (56%) of pure phenyl acrylate,[3] b.p. 65° (1 mm.), $n^{20}D$ 1.5210. The bottom layer consists of trifluoroacetic acid and water from which the CF_3COOH can be recovered as the sodium salt by neutralization with sodium hydroxide and evaporation to dryness on the steam-bath.

Preparation of 1,1-Dihydroperfluorobutyl Acrylate.—Using almost the same procedure, 1,1-dihydroperfluorobutyl alcohol was esterified with glacial acrylic acid in yields of 85–90%. The 1,1-dihydroperfluorobutyl acrylate had the following physical properties, b.p. 51° (50 mm.), $n^{20}D$ 1.3317, d^{20}_4 1.409. Anal. Calcd. for $C_7H_5O_2F_7$: C, 33.1; F, 52.4. Found: C, 33.1; F, 52.4.

(3) E. M. Filachione, J. H. Lengel and C. H. Fisher, ibid., 66, 494 (1944).

CONTRIBUTION No. 62 FROM THE
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The Preparation of Tris-acetylacetone–Rhodium-(III) and –Iridium(III)

BY F. P. DWYER AND A. M. SARGESON
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No acetylacetone complexes of rhodium or iridium in any valency state appear to have been described. The tervalent complexes have been prepared in connection with the study of the optical properties of non-electrolytic complexes. Rhodium(III) hydroxide or sodium rhodate(III) failed to react with acetylacetone. Small amounts of the compound were obtained by refluxing sodium hexachlorhodate(III) with sodium acetylacetonate but the best results by heating a mixture of rhodium(III) nitrate with acetylacetone at pH 4. The iridium compound was obtained in small yield from iridium(III) hydroxide. An unstable reddish water-soluble substance of unknown composition also resulted. This was possibly the acid $H[Ir(OH)_2(Aca)_2]$.

Tris-acetylacetone–rhodium(III).—Rhodium(III) nitrate solution (0.1 g. Rh) in 0.2 N nitric acid (10 ml.) was neutralized with sodium bicarbonate solution (10%) to pH 4. At this acidity the light yellow hydroxide (or basic nitrate) just commenced to separate. Acetylacetone (5 ml.) was added and the mixture refluxed. After a few minutes orange-yellow crystals started to separate, the pH of the mixture falling. After 30 minutes the pH was readjusted and the refluxing continued for a further 15 minutes. The substance after crystallization from aqueous methanol gave orange-yellow monoclinic plates, m.p. 260°, yield 0.3 g., 75%) sublimed at 240° at 1.0 mm. pressure, and decomposed at 280° forming a rhodium mirror. The substance was insoluble in water, slightly soluble in alcohol and petroleum ether, but easily soluble in benzene and chloroform. It was stable to boiling dilute acids and 10% aqueous caustic soda.