t-butyl ions or octyl ions appears to be slow. The present experiments show that gaseous ionic alkylation may be studied in detail by high-pressure mass spectrometry and suggest further studies to determine more precise information about the individual steps in the processes.

The Anodic Oxidation of Organic Compounds. III. The Effect of Electrolyte on Electrochemical Methoxylation and Dimerization of N,N-Dimethylaniline

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Received June 16, 1967

Abstract: Electrode kinetic data for N,N-dimethylaniline (DMA) oxidation in methanol employing potassium hydroxide or ammonium nitrate as electrolytes show the reaction order to be fractional with respect to DMA due to adsorption. Furthermore, one electron is transferred in the rate-controlling step for each of these systems as determined from Tafel plots. Mechanisms are proposed which depict the importance of adsorption of DMA in the formation of N-methoxymethyl-N-methylaniline from the DMA–potassium hydroxide–methanol system and of N,N,N′,N′-tetramethylbenzidine (TMB) from the DMA–ammonium nitrate–methanol medium.

The anodic oxidation of tertiary amines in methanol has been shown[1] to give products with structures indicating the importance of adsorption of the electroactive species on the anode. In one example, N,N-dimethylaniline (DMA) was methoxylated, affording N-methoxymethyl-N-methylaniline (I). On further oxidation, N,N-bis(methoxymethyl)aniline (II) was obtained. No N-dimethoxymethyl-N-methylaniline (III) was detected.

$C_6H_5N(CH_3)CH_2OCH_3$
I

$C_6H_5N(CH_2OCH_3)_2$
II

$C_6H_5N(CH_3)CH(OCH_3)_2$
III

In contrast to the electrochemical oxidation of DMA in methanol are the results reported for other solvents. Electrochemical kinetic studies of DMA oxidation in aqueous acid[2–7] were initially interpreted in terms of a two-electron transfer forming a dication with a reaction order for DMA of unity.[8,9] Since the establishment of new diagnostic criteria for cyclic voltammetric studies of charge-transfer processes with coupled chemical reactions, Adams and co-workers[5] have reinterpreted their work in aqueous acid in terms of a one-electron oxidation followed by a fast chemical reaction. In anhydrous acetic acid,[10] the reaction order is two for DMA with one electron involved in the rate-controlling step.

Similar studies have now been carried out for DMA in methanol containing potassium hydroxide and ammonium nitrate electrolyte. Under conditions of controlled potential electrolysis[11] at 1.20 v *vs.* the saturated calomel electrode (sce), the oxidation of DMA in the potassium hydroxide–methanol solution gave the methoxylated product I. Changing the electrolyte to ammonium nitrate, however, provided TMB as the mononitrate salt. Thus the effect of ammonium nitrate on the electrochemical kinetics of DMA oxidation has also been included here.

Current–voltage curves (Figure 1) for the background oxidation of the solvent demonstrated that the more acidic ammonium nitrate–methanol system was oxidized about 0.5 v more anodic than the corresponding potassium hydroxide–methanol solution. On addition of DMA, oxidation occurred at a lower potential, signifying that solvent or electrolyte oxidation was not involved.

Tafel plots of log current density against potential are shown for the low current density regions in Figure 2. The slopes of the linear regions were each 117 mv/decade, implying that one electron was transferred in the rate-determining step, assuming a symmetry factor of 0.51.

The log–log plots of current against concentration for DMA oxidation in solutions 0.5 *M* in each electrolyte are shown in Figure 3. Determination of the reaction order from the slopes of the linear regions gave values of 0.51 and 0.64 for the potassium hydroxide and

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(8) The reaction order may be obtained from the slope of the log–log plot of current against concentration at constant potential, while the slope of the log current density–potential curve (Tafel plot) gives the value $\beta zF/2.30RT$ where R is the gas constant, T is the absolute temperature, β is the symmetry factor (usually 0.5), z is the number of electrons transferred up to and including the rate-determining step, and F is the Faraday. Further details may be found in ref 9.

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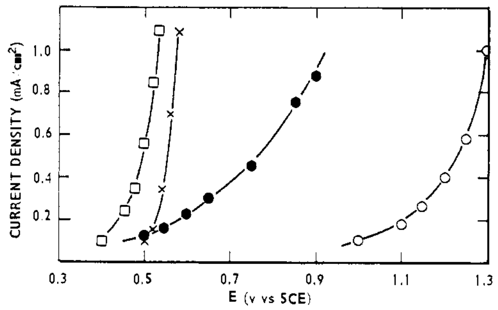

Figure 1. Current–voltage curves: ● 0.5 M KOH–CH_3OH; ○ 0.5 M NH_4NO_3–CH_3OH; □ 0.165 M DMA IN 0.5 M KOH–CH_3OH; × 0.165 M DMA in 0.5 M NH_4NO_3–CH_3OH.

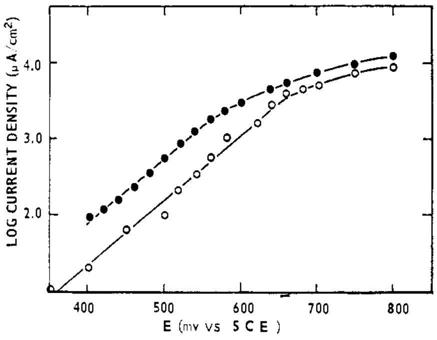

Figure 2. Log current density–potential curves for anodic oxidation of N,N-dimethylaniline (0.165 M): ● in 0.5 M KOH–CH_3OH; ○ in 0.5 M NH_4NO_3–CH_3OH.

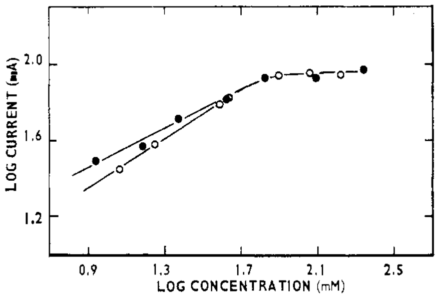

Figure 3. Log–log plots of current against concentration of DMA. Oxidation at E = 1.20 v $vs.$ sce: ● in 0.5 M KOH–CH_3OH; ○ in 0.5 M NH_4NO_3–CH_3OH.

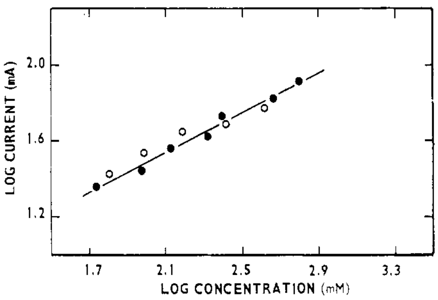

Figure 4. Log–log plots of current against concentration of electrolyte (●, KOH; ○, NH_4NO_3) in DMA (0.042 M)–CH_3OH at E = 1.20 v $vs.$ sce.

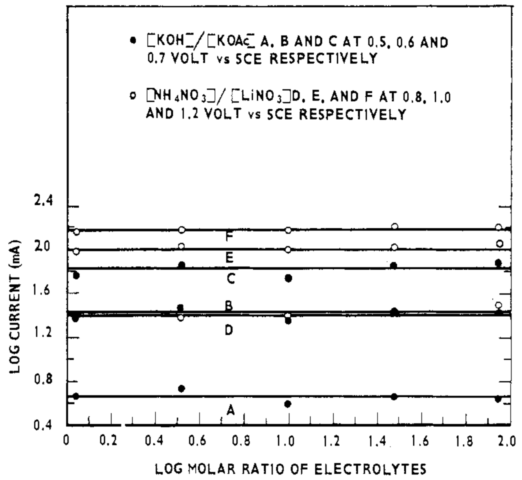

Figure 5. Log–log plot of current against ratio of concentration of electrolytes at 0.5 ionic strength, 0.042 M DMA, 20°.

ammonium nitrate systems, respectively, at 1.20 v $vs.$ sce. In the case of the reaction in ammonium nitrate–methanol, the background is negligible compared to DMA oxidation at 1.20 v. With methanolic potassium hydroxide, the background is appreciable at 1.20 v, but a reaction order plot having the same slope and form has been obtained at 0.50 v where solvent oxidation is insignificant. The plateau ($d(\log i)/d(\log c) = 0$) observed in the reaction order plots was independent of convection over a wide range of stirring rates. While these numbers represent the reaction order for DMA oxidation, they are not necessarily related to the molecularity of the reaction.[9] Interestingly, the apparent reaction orders for the electrolytes obtained from Figure 4 were also fractional, both with a value of 0.54. However, the log current-log concentration ratio plots (Figure 5) for the electrolyte pairs ammonium nitrate–lithium nitrate and potassium hydroxide–potassium acetate, determined at constant ionic strength and at several constant potentials indicated that the fractional order in electrolyte was due to a nonspecific salt effect upon the double layer. This effect probably occurred through the repulsion of a positively charged intermediate at low electrolyte concentration becoming less significant at higher electrolyte concentration.

Using thin layer electrolysis at constant current,[12,13] the number of electrons, n, involved in the over-all electrode reaction has been determined in the case of DMA oxidation in 0.5 M ammonium nitrate solution. Two breaks in the potential–time curve were observed with current densities in the range of 75–150 μa cm^{-2}, each corresponding to a one-electron process per molecule of reactant DMA. The first reaction is probably the oxidation of DMA to tetramethylbenzidine. The second may be due to the further oxidation of TMB to its dication[4,10] occurring in the restricted volume of the thin layer cell. The products of this second reaction were not isolated in the bulk electrolyses. Similar studies with the 0.5 M potassium hydroxide electrolyte were not possible because of interference from oxidation of the electrolyte solution.

Discussion

The fractional reaction orders and limiting current observed in the reaction order plots (Figure 3) are indicative of the reactant obeying a Temkin adsorption

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isotherm with surface saturation[14] prior to charge transfer. Similar effects have been observed by Bagotskii and Vasilyev[15] in their studies of the oxidation of a variety of organic substances. Thus, in proposing a general mechanism of the type

$$\text{DMA} \rightleftharpoons \text{DMA (adsorbed)} \xrightarrow{-e} \text{products}$$

the current will depend on the concentration of reactant and on the potential according to an equation such as

$$i = k \exp(\alpha f\theta) \exp(\beta FE/RT)$$[16]

For the Temkin adsorption isotherm

$$f\theta = \ln Kc$$

where θ is the fraction of the surface covered, $f = (1/RT)[\mathrm{d}(\Delta G_\theta°)/\mathrm{d}\theta]$, $\Delta G_\theta°$ is the free energy of adsorption at coverage θ, K is the equilibrium constant, α is the nonelectrochemical transfer coefficient for adsorption, and c is the bulk concentration of adsorbate. Then $i = Kc^\alpha \exp(\beta FE/RT)$ and the reaction order is given by

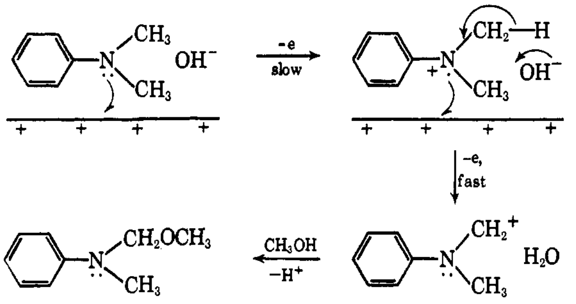
$$\left(\frac{\mathrm{d}\ln i}{\mathrm{d}\ln c}\right)_{\mathrm{E}} = \alpha$$

Frequently, $\alpha = 1 - \beta = 0.5$,[16] in agreement with the results found here. In the region where $(\mathrm{d}\ln i/\mathrm{d}\ln c)_{\mathrm{E}} = 0$, the current is independent of the convection rate and the reaction must proceed through an adsorbed intermediate. A similar treatment using the Freundlich isotherm, wherein

$$\theta = Kc^{1/n}$$

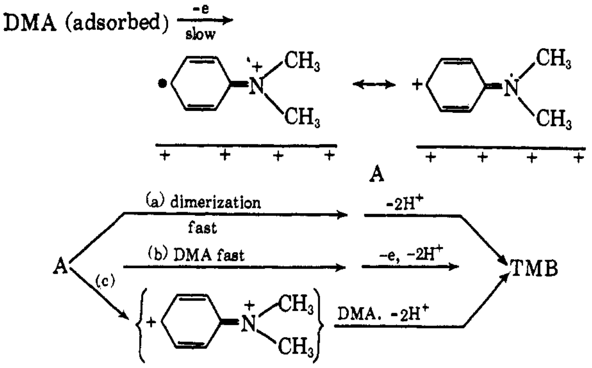
with $n = 2$ would lead to equivalent results.

The diversity in products may be explained in terms of mechanisms incorporating the pH of the solution. The function of the basic medium (eq 1) is then to assist deprotonation of the adsorbed cation radical formed in the rate-determining step. Loss of a second electron followed by solvolysis of the resultant cation would lead to N-methoxymethyl-N-methylaniline (I). In the absence of base-assisted deprotonation, the adsorbed cation radical (eq 2) may only undergo a dimer-forming reaction (eq 3a–c). The kinetic data do not allow distinction among the three proposed routes. Mechanism 3a has been proposed[10] for TMB formation in anhydrous acetic acid.



(1)

The results in eq 2 and 3 clearly demonstrate the importance of the electrolyte in electroorganic reactions. There are several other examples in the literature wherein the nature of the electrolyte may be product determining: the anodic methoxylation of negatively substituted furans must be carried out with sulfuric acid as electrolyte;[17] 1,2,4-trimethoxybenzene undergoes methoxylation in potassium hydroxide–methanol solution,[18] but dimerization in dilute aqueous sulfuric acid;[19] dimethylamides are alkoxylated in poor yield using sodium alkoxide, but in good yield employing ammonium nitrate as the electrolyte;[20] stilbene is methoxylated using sodium methoxide as electrolyte, but with ammonium perchlorate the reaction product is mainly benzaldehyde.[21]



(2)

(3)

Experimental Section

Controlled potential electrolyses and electrode kinetic measurements were carried out at 20° using a one-compartment glass cell of 300-ml volume. A glass joint fitting had provision for a nitrogen gas bubbler, thermometer, two smooth platinum electrodes (12.5 cm^2 each), and an opening for connection of the sce reference electrode (Beckman sleeve type) and exit gas. Rapid stirring was employed using a magnetic stirring bar. A Keithly Model 610A electrometer was used to measure the potential of the working anode against a saturated calomel electrode positioned within 2 mm of it. A Hewlett-Packard Model 412A dc vacuum tube voltmeter was used for current determination. An Acromag integrator (Acromag, Inc., Detroit, Mich.) functioned as a coulometer. In a typical electrolysis at an anode potential of +1.20 v *vs.* sce, the cell voltage was 3 v and the current 260 ma. The magnitude of these variables is well below the output capability (±40 v and ±6 amps) of the potentiostat (Instruments and Communications, Inc. Wilton, Conn.) employed in this study.

Controlled Potential Electrolysis of DMA. A. In Potassium Hydroxide Solution. A solution consisting of 4.0 g of DMA in 100 ml of 0.5 *M* methanolic potassium hydroxide was electrolyzed at a controlled anodic potential of 1.20 v *vs.* sce. After 1588 coulombs had been passed, the solution was concentrated at reduced pressure at 30–40° to a thick paste. This was taken up in 100 ml of water and extracted with three 50-ml portions of diethyl ether. The combined ether extract was dried over anhydrous magnesium sulfate, filtered, and the solvent evaporated leaving 4.0 g of crude oil. Examination of this material by gas chromatography (Aerograph Model A-100) on 0.3% SE-30 on glass beads, and comparison of retention times with authentic samples demonstrated that the oil was a mixture of DMA (90.9%) and N-methoxymethyl-N-methylaniline (9.1%).

B. In Ammonium Nitrate Solution. A solution of 2.0 g of DMA in 100 ml of 0.5 *M* methanolic ammonium nitrate was electrolyzed at a controlled anodic potential of 1.20 v *vs.* sce until 715 coulombs had been passed. During the reaction the solution became deep blue-green, and a dark green solid was deposited on the anode. The solid (0.33 g) was removed from the electrode and crystallized once from 20 ml of methanol to yield pale yellow crystals, mp[22] 194–196°. The nmr spectrum in dimethyl sulfoxide was consistent with the

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structure for N,N,N′,N′-tetramethylbenzidine mononitrate salt. **Anal.** Calcd for $C_{16}H_{21}N_3O_3$: C, 62.08; H, 7.22; N, 14.32. Found: C, 61.81; H, 6.83; N, 14.00.

The solution was not examined for further products.

Acknowledgments. The authors wish to thank Professor B. E. Conway and Dr. A. K. Hoffmann for valuable discussion.

Organic Syntheses by Means of Noble Metal Compounds. XXXIV.[1] Carbonylation and Decarbonylation Reactions Catalyzed by Palladium

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Received June 12, 1967

Abstract: The palladium-catalyzed decarbonylation of acyl halides and aldehydes to form olefins has been studied. The carbonylation of olefinic compounds and the decarbonylation of acyl halides and aldehydes as well as the Rosenmund reduction are discussed from a common mechanistic standpoint.

Recently the usefulness of palladium in organic syntheses has attracted much attention. The well-known Wacker process to form carbonyl compounds from olefins is a typical example.[2] In addition, we have shown that palladium is a versatile catalyst for the carbonylation of various compounds. For example, an olefin–palladium chloride complex is carbonylated at room temperature to form β-chloroacyl chloride with the reduction of divalent to zero-valent palladium.[3] Furthermore, metallic palladium catalyzes the carbonylation reaction of olefins to form saturated esters[4] and aldehydes,[5] and a brief mechanistic discussion has been given.[6,7] Also diolefins,[8–10] allylic compounds,[11,12] and acetylenic compounds[13–15] are carbonylated. Based on the mechanism of the carbonylation and an assumption that the carbonylation reaction is reversible, we expected that decarbonylation of aldehydes and acyl halides should be catalyzed by metallic palladium. We now have established that the decarbonylation of aldehydes and acyl halides can be carried out in the presence of a catalytic amount of metallic palladium and the scope of the reaction is described in this paper.

The formation of a true palladium carbonyl comparable to nickel carbonyl has not been reported and only carbonyl derivatives of palladium are known.[16,17] The metallic palladium catalyzed carbonylations proceed in the presence of some kind of hydrogen source. Hydrogen halides and molecular hydrogen are found to be satisfactory analogous to the nickel carbonyl catalyzed reaction, in which addition of hydrogen halide to form a hydrogen–nickel bond is assumed as prerequisite of the catalysis.[18] The question as to how the solid catalyst like metallic palladium can catalyze both carbonylation, which is usually possible only by complex transition metal carbonyl catalysts under homogeneous conditions, and decarbonylation is considered in this paper.

Results

Decarbonylation of Acyl Halides. In the presence of a catalytic amount of metallic palladium, it was found that acyl halides can be decarbonylated smoothly to give olefins, carbon monoxide, and hydrogen halides. The decarbonylation reaction of acyl halides to form olefins is a new reaction, and it is useful in organic syntheses to degrade acid derivatives by one carbon.

Higher aliphatic acyl chlorides and bromides were decarbonylated in high yields to give olefins having one less carbon atoms when they were heated with a catalytic amount of metallic palladium at 200°. Palladium black or palladium on carbon prepared for hydrogenation is satisfactory as the catalyst. The olefins produced were a mixture of isomeric inner olefins even when the olefins were distilled off from the reaction medium as soon as they were formed. The decarbonylation of acyl halides which have no β hydrogen gave alkyl halides with one less carbon atom. For

$$RCH_2CH_2COX \longrightarrow RCH{=}CH_2 + CO + HX$$

$$RCOX \longrightarrow RX + CO$$

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