(19) Although parallelism of indicator ionization curves is only strictly required for overlapping pairs of bases in the acidity function approach, examination of ionization ratio behavior generally shows steady trends in the slope of log *I* *vs.* acid concentration.

(20) J. F. Bunnett, *J. Amer. Chem. Soc.*, **83**, 4956, 4968, 4973, 4978 (1961); see also ref 17, Chapter 4.

(21) K. Yates and M. F. Goldman, unpublished results.

(22) K. Yates, *Accounts Chem. Res.*, **4**, 138 (1971).

A Sensitive Probe for Double Layer Structure. Potential Dependent Competitive Cyanation and Methoxylation of 1,4-Dimethoxybenzene

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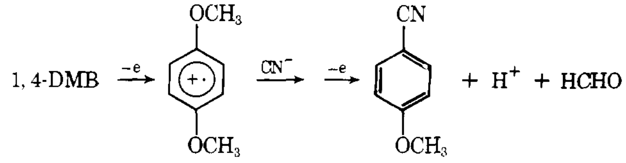
Abstract: It is possible to determine the relative concentrations of nucleophiles at the electrode from products of electrolysis using competitive reactions. The electrochemical oxidation of 1,4-dimethoxybenzene (1,4-DMB) in NaCN-CH_3OH solution affords three primary products, as well as a secondary methanolysis product. The current efficiencies of two products (**1** and **2**) are highly potential dependent, while the current efficiency of the third (**3**) taken together with its methanolysis product (**4**) is found to be independent of potential. Current-potential data support a cation radical mechanism. From the rate expressions it is shown that the concentrations of reactive cationic species formed on electron transfer provide sensitive probes for the relative concentration of nucleophiles (CN^-/CH_3O^-) in the double layer. The dependence of the current efficiencies of **1** and **2** on potential is shown to be related to (CN^-/CH_3O^-) which significantly increases in value as the electrode potential is made positive. In contrast to the above, electrolysis of 1,4-DMB in KOCN-CH_3OH solution provides the quinone diketal (**2**) as the sole aromatic-derived product. The observation is consistent with the order of reactivity of nucleophiles in methanolic solution as $CH_3O^- > CN^- > OCN^- > CH_3OH$.

Among the electrochemical reaction variables[2] requiring considerably more elucidation than is presently available for a detailed understanding of electroorganic synthesis is the role of the electrode potential as it influences both electrochemical adsorption and concentrations of reactive species at the electrode. Certainly studies over the past decade have provided improved models of the region of solution adjacent to the electrode, i.e., the double layer,[3] and increased our knowledge substantially regarding reaction pathways of organic compounds at electrodes.[4-6] Yet most investigations combining organic electrochemistry with an understanding of adsorption processes have dealt with fuel cell-type reactions[7,8] where little can be learned mechanistically from the nature of the simple end products, CO_2 and H_2O. It is a primary purpose of this paper to show that a great deal of insight can be gleaned concerning the potential dependence of concentrations of species at the electrode from the structure and yields of products formed in competitive reactions.

The electrochemical oxidation of 1,4-dimethoxybenzene at a Pt electrode in CH_3CN containing Et_4NCN as supporting electrolyte was shown by Andreades and Zahnow[9] to lead to anisonitrile (**1**) in high yield. Further evidence indicated that the reaction mechanism probably goes through a cation radical route as in eq 1. Likewise, Weinberg and Belleau[10] showed that electrochemical methoxylation of 1,4-DMB in CH_3OH containing KOH as supporting electrolyte gives the quinone diketal (**2**) in about 65% current efficiency (CE). Recently[11] this reaction was shown conclusively to proceed through a cationic route, likely occurring according to eq 2. Consequently, electrooxidation of 1,4-DMB in NaCN-CH_3OH at Pt should afford both of the above products (**1** and **2**) since this electrolyte solution will contain both CN^- and CH_3O^- ions. More importantly, if adsorption processes are involved, it was considered that this system should provide information on the relative (if not absolute) concentration of nucleophiles at the electrode by studying the products (**1** and **2**) as a function of potential.



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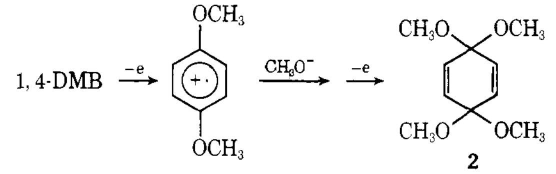

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(2)

Results

Products. Electrolyses were conducted in 0.5 *M* NaCN-CH_3OH in a three-compartment H-cell in the potential region +1.00 to +1.70 V vs. SCE at Pt electrodes. Four major products were identified by GC and analytical methods in a total of about 100% CE. Besides **1** and **2**, 3-cyano-3,6,6-trimethoxy-1,4-cyclohexadiene (**3**) was found, in addition to some of its methanolysis derivative (**4**). The latter is not a direct electrochemical product but is formed in base catalyzed reaction of **3**.[12] A trace of 4,4-dimethoxy-2,5-cyclohexadienone (**4a**) was also noted. It is of interest that no evidence could be obtained for the presence of the dicyanodiene (**5**) in the reaction product mixture, although this may be a high retention-time product observed in the GC in trace quantity, but not separated.

Products **3** and **4** have not been reported previously, nor was product **5** observed by Andreades and Zahnow[9] in their

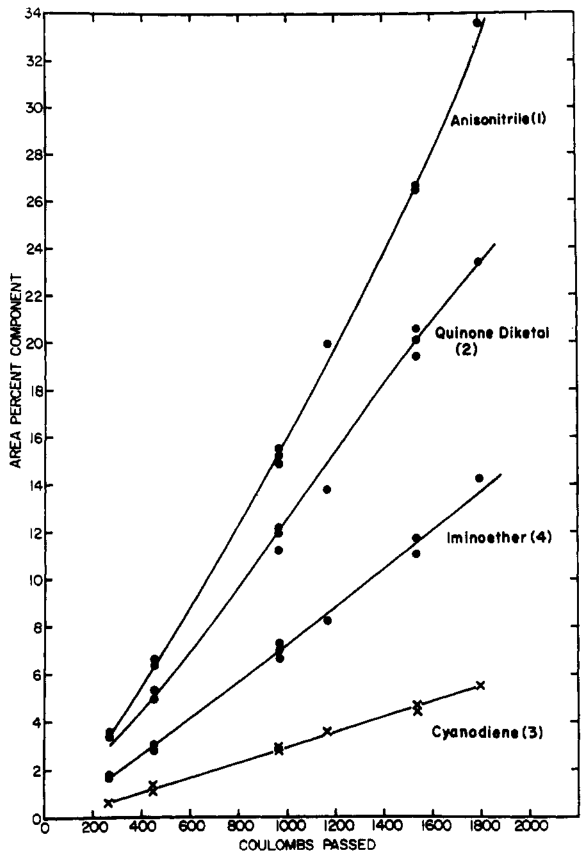
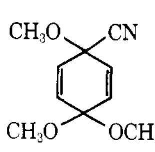


Figure 1. Plots of area percent components (by GC) in electrolysis of 1,4-DMB (0.0010 *M*) in 0.50 *M* NaCN-CH_3OH at Pt at 1.30 V vs. SCE as a function of coulombs passed.



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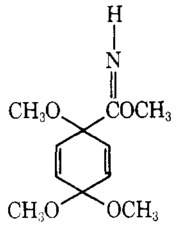

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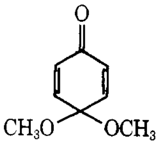

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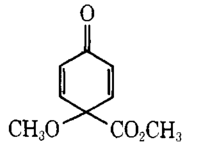

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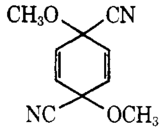

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work. The structure proof of 3 and 4 rests on elemental as well as spectroscopic data and on the conversion by hydrolysis in aqueous acid solution of the imino ether (4) to the cyclohexadienone **4b**, also previously unreported to our knowledge.

Attempted electrooxidation of anisonitrile (1) under similar conditions demonstrated that 1 is not converted to any of the other products, since 1 was recovered quantitatively even at an electrolysis potential of +2.5 V vs. SCE. Likewise the three primary products (**1, 2** and **3**) were found to be chemically noninterconvertible within experimental error by allowing the reaction solution to stand for 24 hr without electrolysis and examining the solution periodically by GC. During this period, a slow conversion of 3 to 4 did occur.

Figure 1 is a plot of GC results as area percent of component product vs. the number of coulombs (C) passed for an electrolysis conducted at 1.30 V vs. SCE. It is seen that the products are formed in a linear manner with the number of coulombs, further providing evidence for noninterconversion of the products. The chemical methanolysis of 3 is seen to be also linearly related to the number of coulombs.

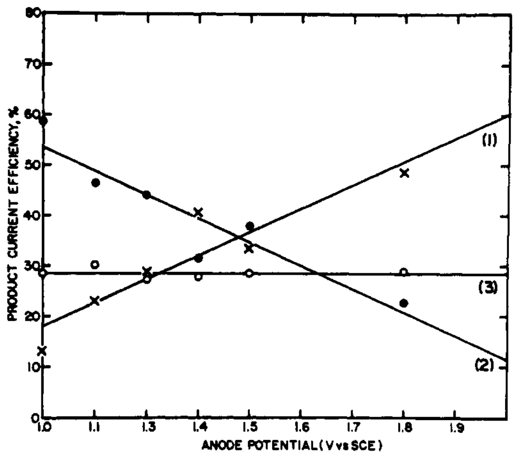


Figure 2. Plots of current efficiency of products from 1,4-DMB (0.0010 *M*) Electrolysis as a function of anode potential (at Pt (10 cm^2) in 0.50 *M* NaCN-CH_3OH at 15°): (1) anisonitrile (**1**); (2) quinone diketal (**2**); (3) cyanodiene (**3**) + imino ether (**4**).

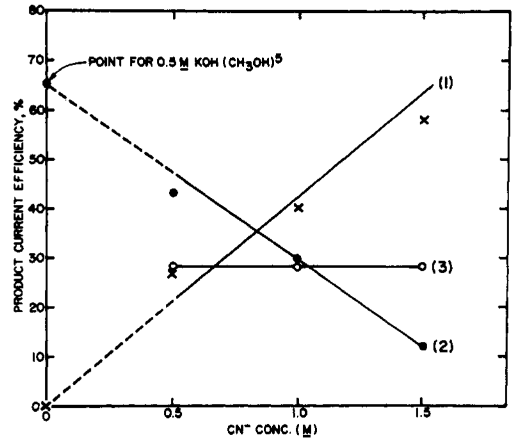


Figure 3. Plots of current efficiency of products from 1,4-DMB (0.0010 *M*) electrolysis as a function of cyanide ion concentration (at Pt (10 cm^2) in 0.50 *M* NaCN-CH_3OH at 15° at 1.40 V vs. SCE): (1) anisonitrile (**1**); (2) quinone diketal (**2**); (3) cyanodiene (**3**) + imino ether (**4**).

The results of controlled potential electrolysis (CPE) of 1,4-DMB in 0.5 *M* NaCN-CH_3OH at 15° are shown in Figure 2. Each point represents an average of two experiments conducted at the same potential. The plotted curves (1, 2, and 3) are the corresponding least-squares lines. Thus the CE of anisonitrile (**1**) and of quinone diketal (**2**) are highly potential dependent. The CE of cyanodiene (**3**) taken together with its methanolysis product (**4**) is independent of potential.

Of further interest are the results obtained with increased cyanide ion concentration, namely 1.0 and 1.5 *M* NaCN-CH_3OH solutions. These observations are plotted in Figure 3. Note that as the CN^- ion concentration is increased, the CE of anisonitrile (**1**) formation is increased, whereas the CE of quinone diketal (**2**) is decreased. Significantly curve 1 at zero CN^- ion concentration predicts no anisonitrile. Curve 2 predicts a 65% CE of quinone diketal. The former result would be experimentally obvious; however, the latter result is actually observed experimentally over a wide range of potentials more positive than about 1.3 V.[11] Curve 3 is independent of CN^- ion concentration from 0.5 *M* increasing to 1.5 *M*. Below 0.5 *M* the CE of 3 should tend toward zero; however, no experiments were conducted at less than 0.5 *M* NaCN to verify this point.

Table I

Potential (V vs. SCE)	Anode	1	2	3
1.0	Pt	18.0	58.5	28.4
	C	27.7	35.0	37.3
1.4	Pt	33.5	38.0	28.4
	C	35.2	26.9	38.2

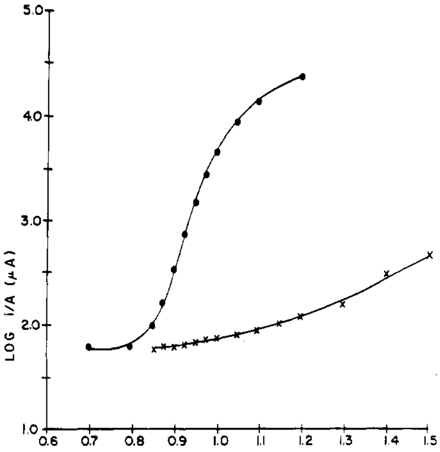


Figure 4. Tafel plot of oxidation of 1,4-DMB (0.100 *M*) in 0.5 *M* NaCN-CH_3OH at Pt (10 cm^2) at 15° (solution magnetically stirred): ×, 0.5 *M* NaCN-CH_3OH; ● 1,4-DMB added.

Two experiments were carried out at a carbon anode (Atomergic Vitreous Carbon rod, 50 × 3 mm (diameter)) in 0.5 *M* NaCN-CH_3OH solution at 15° to compare the role of anode materials. The current efficiencies of the products at 1.0 and 1.4 V vs. SCE are as shown in Table I. It is seen that the CE of **3** again appears to be relatively constant with potential; however, **3** is formed in about 10% higher CE at C than at Pt. On the other hand considerably more quinone diketal **2** and somewhat less anisonitrile **1** is obtained.

Two electrolyses at controlled potential of 1,4-DMB in KOCN-CH_3OH at a Pt anode were conducted to see whether OCN^- ion could be trapped by cationic species. In both cases only the quinone diketal (**2**) was formed in nearly quantitative CE with no evidence for the presence of isocyanate or carbamate products formed. Thus although OCN^- like CN^- ion in methanol solution increases the useful potential region to about +1.7 V compared to other supporting electrolytes,[13] OCN^- does not enter into the nucleophilic reactions.

Current-Potential Data. Figure 4 presents current-potential curves in the form of Tafel plots (log current density vs. potential) for oxidation of 0.5 *M* NaCN-CH_3OH and for the same solution with added 1,4-DMB (0.10 *M*). The slope of the rising linear portion of the latter curve is 108 mV/decade, providing evidence that one electron is probably transferred from 1,4-DMB in the rate-determining step.[13] From controlled potential electrolyses of 1,4-DMB in NaCN-CH_3OH at Pt over the range 1.0–1.7 V, a coulombic value of n = 2.0 electrons/molecule of 1,4-DMB was obtained. The peak potential (E_p) of 1,4-DMB (5 × 10^{-3} *M*) in 0.5 *M* NaCN-CH_3OH from a cyclic voltammetric[14] experiment at Pt is 1.1 V vs. SCE, showing only one irreversible peak. Andreades and Zahnow[9] found two peaks at Pt for 1,4-DMB oxidation in CH_3CN-Et_4NClO_4 solution at 1.15 and 1.75 V vs. SCE.

Figure 5 is a plot of log current vs. log concentration of 1,4-DMB in 0.5 *M* NaCN-CH_3OH. The data were taken for a magnetically stirred solution and were shown to be independent of the rate of stirring. The lower portions of the curves exhibited slopes in the range 0.4–0.7. For Temkin adsorption behavior a slope of about 0.5 would be indicated.[12] At higher concentrations of 1,4-DMB the curves tend to be considerably less dependent on concentration, suggesting that saturation coverage of 1,4-DMB occurs, Hence some evidence for adsorption of 1,4-DMB prior to charge transfer is provided.

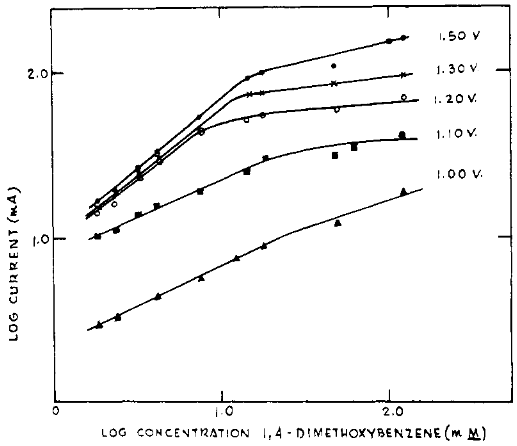


Figure 5. Log-log plots of current vs. 1,4-DMB concentration in 0.50 *M* NaCN-CH_3OH at Pt (10 cm^2) at 15°.

Discussion

Since electrochemical oxidation of 1,4-DMB is expected to provide various cationic species as intermediates, it is pertinent to consider the nonelectrochemical literature as it relates to nucleophilic reactions in methanolic solution.

Fortunately for our needs, Ritchie and coworkers[15] have presented some unusual insights as well as a new understanding of nucleophilic reactions with carbonium ions in a variety of solvents including methanol. In the cited work, the reaction kinetics of relatively stable carbonium ions were examined including triarylmethyl cations, aryldiazonium ions, and tropylium ions. Their entire kinetic data could be correlated to a rather simple equation (eq 3),

$$\log[k_n/k_{H_2O}] = N_+ \tag{3}$$

where k_n is the rate constant for reaction of the cation with a given nucleophile in a particular solvent, k_{H_2O} is the rate constant of water in water, and N_+ is a parameter characteristic of the nucleophile in the particular solvent and is independent of the cation. Thus N_+ for CH_3OH in CH_3OH was found to be 0.5, 5.9 for CN^- in CH_3OH, and 7.5 for CH_3O^- in CH_3OH.

Using these data, it may be shown that *relatively stable carbonium ions will react about 40 times faster with methoxide ion than with cyanide ion in methanol solution.* Any reaction with methanol in the presence of these nucleophiles should be insignificant. A further point relative to our electrochemical studies is that methanolic cyanide solutions contain an abundant concentration of methoxide ion as a result of the equilibrium (eq 4). Ritchie et al.[16] have estimated

$$CN^- + CH_3OH \rightleftharpoons CH_3O^- + HCN \tag{4}$$

mated $K_b \approx 10^{-3}$ *M* for eq 4. Thus a 0.50 *M* NaCN-CH_3OH solution will actually contain approximately 0.41 *M* cyanide and 0.09 *M* methoxide ions. It is thus not surprising therefore, that products both of cyanation and methoxylation result from the electrochemical oxidation of 1,4-DMB.

Three mechanistic schemes are proposed to account for the electrochemical behavior of 1,4-DMB, the observed products, and their CE vs. potential dependence.

Mechanism I. A cation radical/dication mechanism suggests that the product distribution observed with potential is a function of the concentration of the cation radical of 1,4-DMB, produced at low positive potentials, as well as the concentration of the dication of 1,4-DMB formed at more positive potentials (eq 5 and 6). The highly reactive

$$R \overset{E_1}{\rightleftharpoons} R^{\cdot+} + e \tag{5}$$

$$R^{\cdot+} \overset{E_2}{\rightleftharpoons} R^{2+} + e \tag{6}$$

dication would be less discriminating than the cation radical. Then because cyanide is present at about five times the methoxide ion concentration, greater yields of the cyanation products would be expected as the electrode potential is increased more positively.

In NaCN-CH_3OH solution only one irreversible peak in the cyclic voltammogram is observed at 1.1 V vs. SCE for the cation radical. The absence of a second oxidation peak in CH_3OH for the dication eliminates positive proof of its existence. A search of the literature[17] for examples to support mechanism I further tends to negate this route. Reasonably well-established cases in which one- and two-electron oxidations of aromatics and olefins are involved demonstrate that at the potential corresponding to the second electron transfer (i.e., to the formation of the dication) the products change markedly. Figure 2 suggests no such discontinuity.

Mechanism II. A disproportionation sequence (eq 7 and 8) would better account for the results. Here, 1,4-DMB gives rise to the cation radical which undergoes disproportionation according to

$$R \rightleftharpoons R^{\cdot+} + e \tag{7}$$

$$2R^{\cdot+} \rightleftharpoons R + R^{2+} \tag{8}$$

Considerable evidence has accumulated for disproportionation of cation radicals in support of this scheme.[17] We do not discount mechanism II; however, until adequate proof of a disproportionation sequence is obtained we prefer mechanism III.

Mechanism III. The cation radical mechanism presented in Scheme I readily explains all of our experimental observations. Here the cation radical of 1,4-DMB (CR) and the cyclohexadienyl cations (**6** and **7**) react competitively with CN^- and CH_3O^- ions. We may denote rate constants as k_1, k_2, k_3, k_4, k_5, k_6, and k_7 and current efficiencies as **1**, **2**, **3x**, **3y** (where **3x** + **3y** = **3**), **6**, and **7**.[18] Thus **3x** and **3y** represent the CE of product **3** formed in the upper and lower branches of Scheme I, respectively. Treating the reactions in Scheme I as a system of parallel reactions[19] the following expressions may be derived.

$$\left(\frac{k_1}{k_2}\right)\left(\frac{CN^-}{CH_3O^-}\right) = \frac{1 + 3x}{2 + 3y} \tag{9}$$

$$\left(\frac{k_3}{k_4}\right)\left(\frac{CN^-}{CH_3O^-}\right) = \frac{3y}{2} \tag{10}$$

$$\left(\frac{k_5}{k_6}\right)\left(\frac{CN^-}{CH_3O^-}\right) = \frac{1}{3x} \tag{11}$$

$$\left(\frac{6}{7}\right) = \left(\frac{3x}{2}\right) \tag{12}$$

$$\text{where } 3x + 3y = 3 = 28.4 \tag{13}$$

We would like to evaluate the relative quantities k_1/k_2, k_3/k_4, k_5/k_6, CN^-/CH_3O^-, and **6**/**7**; however, too few

Scheme I. Cation Radical Mechanism for Competitive Cyanation and Methoxylation of 1,4-DMB

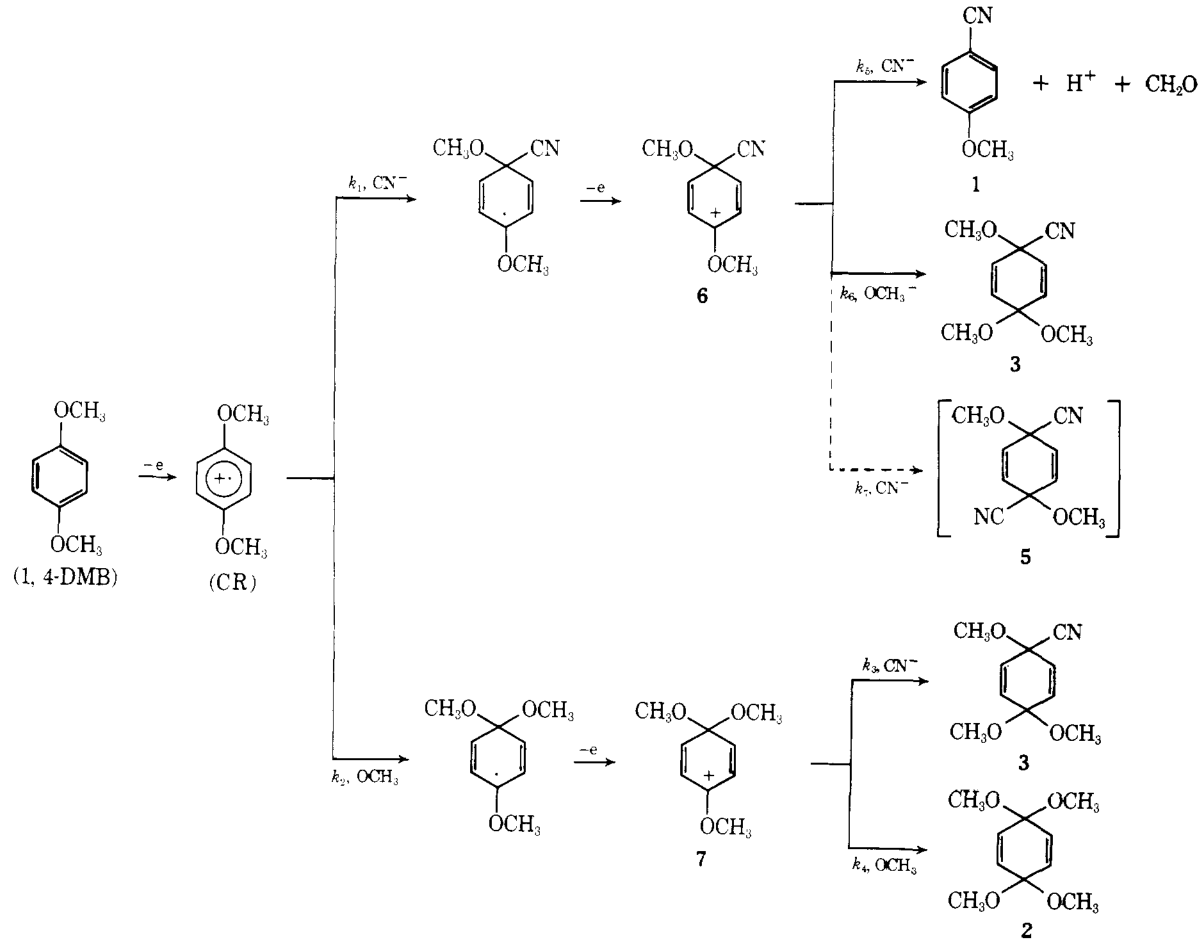


Table II. Solution of Equations 9–13 Assuming $\frac{k_1}{k_2} = \frac{k_3}{k_4} = \frac{1}{40}$

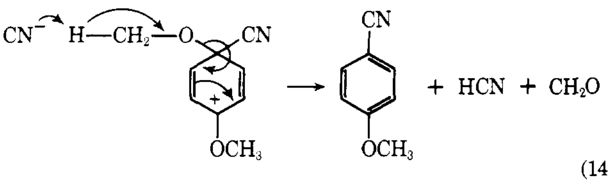
E	k_5/k_6	CN^-/CH_3O^-	**3x**	**3y**	**6**/**7**
1.0	0.14	15	8.8	20	0.16
1.1	0.18	17	7.4	21	0.15
1.2	0.22	20	6.1	22	0.14
1.3	0.27	24	5.1	23	0.13
1.4	0.32	28	4.2	24	0.12
1.5	0.35	33	3.6	25	0.12
1.6	0.35	39	3.4	25	0.13
1.7	0.29	48	3.6	25	0.18

equations are available, and it is necessary to make at least two further assumptions. The following cases covering a wide range of possibilities have been examined: case I, $k_1/k_2 = k_3/k_4 = 1/40$ (see Ritchie[15]); case II, $k_3/k_4 = 1/40$, and the ratio at 0.8 V of $(CN^-/CH_3O^-) = (0.41/0.09)$. (Here it is assumed that the bulk concentration of nucleophiles is equal to that at the electrode at 0.8 V, a potential at which no appreciable current flows (see Figure 4) for oxidation of 1,4-DMB. The ratio of (CN^-/CH_3O^-) can then be compared at all other potentials.); case III, $k_3/k_4 = 1/40$, **3x** = 0, hence **3y** = 28.4; case IV, $k_3/k_4 = 1/40$, **3y** = 0, hence **3x** = 28.4; case V, $k_3/k_4 = 1/40$, **3x** = **3y** = 14.2; case VI, $k_3/k_4 = 1/40$, **3x**/**3y** = 0.10, hence **3x** = 2.6; case VII, $k_3/k_4 = 1/40$, **3x**/**3y** = 10, hence **3x** = 25.8.

Applying the least-squares data interpolated from lines 1, 2, and 3 of Figure 2, and solving for case I, the results shown in Table II are obtained. It is seen that the value of (CN^-/CH_3O^-) increases about threefold from +1.0 to +1.7 V vs. SCE. In addition, over a significant region of potential (1.3–1.7 V) the value of k_5/k_6 is reasonably constant and the distribution of **3** in the two pathways does not vary markedly with potential. The same kind of trend is observed for case II, and for cases III–VII, (CN^-/CH_3O^-) increases with increasing potential (by a factor of about three to four) and k_1/k_2 and k_5/k_6 are reasonably constant. It is apparent from these results that the quantity (CN^-/CH_3O^-) should actually be designated as (CN^-/CH_3O^-), i.e., referring to relative concentrations of these ions at the anode as compared to the bulk.

There is a question of whether nucleophilic reactions occur with cyanide and methoxide *on* the electrode or in the region of solution next to the electrode (i.e., the double layer) extending out from the electrode about 10 Å. Little or no methoxide is on the electrode in methanolic cyanide solution according to current/potential data (including cyclic voltammetry) because almost no oxidation current for methanol or methoxide is observed. Hence we are led to conclude that reaction of methoxide ion with 1,4-DMB cation radical or the cyclohexadienyl carbonium ions (**6** and **7**) occurs in the double layer. The same may or may not be true for cyanide ion; however, since cyanide ion is known to adsorb strongly on Pt,[20,21] it is likely that reaction occurs with available, i.e., unadsorbed, cyanide ion in solution.

The question of how anisonitrile is formed from **6** is an interesting one. Aromatization could occur by either spontaneous loss of the species CH_3O^+ or via a base assisted reaction, namely,



(14)

In the former case, the competitive rate expressions would lead to

Table III. Comparison of Relative Rate Constants

Case	$k_1/k_2{}^a$	$k_3/k_4{}^a$	$k_5/k_6{}^a$	$k_5/k_7 \approx (k_5/k_6)(k_4/k_3)^a$
I	0.025^b	0.025^b	0.27	11
II	0.093	0.025^b	0.17	6.4
III	0.016	0.025^b	∞	∞
IV	0.025^b	0.00	0.17	0
V	0.060	0.025^b	0.15	6.0
VI	0.020	0.025^b	0.43	17
VII	0.54	0.025^b	0.43	17

[a] Average values over the potential region 1.00–1.70 V are given.
[b] Assumed values.

$$k_5/k_6(CH_3O^-) = \mathbf{1/3x} \qquad (15)$$

and in the latter case, eq 11 would result. If eq 15 is used, it is found that k_5/k_6 varies markedly with potential for cases I–VII. On the other hand, we have shown that the value of k_5/k_6 derived from eq 11 is reasonably independent of potential. Consequently we favor base-assisted aromatization[22] via eq 14.

An explanation for the absence of **5** in the product mixture may be obtained by dividing eq 11 by 10, noting that $k_4 \approx k_6$ and $k_3 \approx k_7$, thus

$$\left(\frac{k_5}{k_6}\right)\left(\frac{k_4}{k_3}\right) \approx \left(\frac{k_5}{k_7}\right) \approx \left(\frac{1}{\mathbf{3x}}\right)\left(\frac{2}{\mathbf{3y}}\right) \qquad (16)$$

Table III shows that $k_5 \gg k_7$ for cases I to VII (excluding IV). This taken with the fact that $k_6 > k_7$ ($k_6/k_7 \approx k_4/k_3 \approx 40$)[14] demonstrates that **5** should be formed, but its yield will be low in all likelihood.

Why are the results different at Pt and vitreous carbon? Calculation of the values (CN^-/CH_3O^-) and **6**/**7** for the results at vitreous carbon (cases I, II, and IV–VII) show that these are very nearly twice the value calculated for Pt. Apparently a greater concentration of CN^- is available at carbon compared to Pt over the entire 1.0–1.7 V potential region. This is a curious result in view of strong chemisorption of CN^- ion on Pt.[20,21] One explanation may be that carbon does not adsorb CN^- ion as strongly as does Pt and consequently more CN^- ion is available for nucleophilic reaction at the carbon electrode. Further work is in progress to attempt to clarify this point.

If the cation radical scheme is substantially correct, it seems reasonable to expect that **3** is formed in both branches in significant quantity. Then disregarding cases III and IV as unlikely, it is seen that k_1/k_2 is about equal to or greater than k_3/k_4; i.e., the cation radical of 1,4-DMB is not more stable than the cyclohexadienyl cations **6** and **7**.

Scheme I adequately explains the potential independence of the CE of **3**. At low potential, i.e., low CN^- ion concentration, **6**/**7** is small and **3x** is small but **3y** large. As the potential is increased, the system is balanced by **6** increasing in concentration with a larger value of **3x** occurring.

Consider the results obtained on electrooxidation of 1,4-DMB in 0.5 *M* $KOCN-CH_3OH$ in the light of what has been proposed for reaction in 0.5 *M* $NaCN-CH_3OH$. No products were obtained in which OCN^- ion was trapped. Yet the current-potential curves in $KOCN-CH_3OH$ for oxidation of 1,4-DMB are not too differently displaced compared to the $NaCN-CH_3OH$ solution. Consequently OCN^- ion is probably adsorbed strongly, sufficient to prevent adsorption and hence oxidation of CH_3O^- ion, yet is a very poor nucleophile compared to CH_3O^- or CN^- ion. We may then place the relative order of reactivity of nucleophiles in methanol as $CH_3O^- > CN^- > OCN^- > CH_3OH$, an order which is in essential agreement with Ritchie's work.[15]

In conclusion, it is apparently possible to determine the relative concentrations of reacting species at the electrode by studying the nature of all the products formed and their distribution as a function of potential.

Experimental Section

Preparative electrolyses were conducted in a three-compartment H-cell separated by glass frits.[2,13] The runs were carried out under controlled potential conditions using a PAR Model 173 potentiostat. The contents of the working electrode compartment were stirred magnetically, and the cell was thermostated at 15°. Unless otherwise specified, smooth Pt electrodes (10 cm^2) were used as working and counter electrodes, and an aqueous SCE was employed as reference. Cyclic voltammetric studies were carried out in a one-compartment cell containing a Pt working electrode (1 cm^2), a Pt auxiliary electrode, and an aqueous SCE reference electrode. A PAR Model 170 Electrochemical System was used.

GC analyses and preparative-scale separations were performed with an F&M Model 720 gas chromatograph containing dual 12 ft × ¼-in. stainless steel columns of 20% SE 30 on Anachrome ABS. NMR analyses were carried on a Varian Model HA-100 spectrometer, while mass spectral studies were performed with an AEI MS 12.

1. Preparative Controlled Potential Electrolysis of 1,4-Dimethoxybenzene. The following example gives a typical preparative procedure. The H-cell was equipped with Pt electrodes and SCE reference and contained 0.5 *M* NaCN in CH_3OH. A controlled potential electrolysis was carried out at 1.40 V on 1.38 g (0.0100 mol) of 1,4-dimethoxybenzene dissolved in 100 ml of the anolyte solution, which was stirred magnetically under N_2. After passage of 2140 C (initial current 150 mA, final current 3.6 mA) the anolyte was evaporated down and the residue taken up in 200 ml of ethyl ether, washed with two 50-cm^3 of water, and dried over anhydrous $MgSO_4$. This was then filtered and the filtrate was concentrated *in vacuo* to give 1.40 g of crude product (an oil). GC analysis showed the presence of five major components, an unidentified minor component, as well as a trace of starting material.

Isolation of the various products was performed using preparative GC techniques. These products are listed below in order of increasing retention time: (i) 1,4-dimethoxybenzene (trace, <1%), (ii) 4,4-dimethoxy-2,5-cyclohexadienone (**4a**) (trace <2%), previously identified,[22] (iii) anisonitrile (**1**), (iv) quinone diketal (**2**), previously identified,[9,10] (v) 6-cyano-3,3,6-trimethoxy-1,4-cyclohexadiene (**3**) (This material was isolated containing 15% of anisonitrile as a difficultly separable impurity. Spectral analyses take this impurity into account; the NMR spectrum of this material in CCl_4 exhibited 3 H singlets at δ 3.22, 3.25, and 3.31, and a 4 H A_2B_2 quartet ν_A 6.00, ν_B 6.18, and J_{AB} = 10.6 Hz. The mass spectrum gave M^+ at 195 and a fragmentation pattern consistent with the proposed structure, **3**.), (vi) imino ether (**4**) (This product was isolated as a solid, which on crystallization from hexane-chloroform solution, had mp 71-72°. The NMR spectrum in acetone-d_6 exhibited 3 H singlets at δ 3.16, 3.23, 3.29, and 3.61 ($N{=}COCH_3$), and a 4 H A_2B_2 quartet with ν_A 5.69, ν_B 6.23, and J_{AB} = 10.6 Hz. Ir analysis in CCl_4 solution showed characteristic bands at 3355 (N-H) and 1660 cm^{-1} ($C{=}N$). Anal. Calcd for $C_{11}H_{17}NO_4$: C, 58.12; H, 7.54; N, 6.16. Found: C, 57.82; H, 7.59; N, 6.07. The imino ether was hydrolyzed in dilute aqueous solution to give 4-methoxy-4-carbomethoxy-2,5-cyclohexadienone (**4b**) quantitatively, mp 87-88° (crystallization from cyclohexane-$HCCl_3$). The NMR spectrum in CCl_4 solution exhibited 3 H singlets at δ 3.26 and 3.74, and a 4 H A_2B_2 quartet centered at δ 6.56 with J_{AB} = 10.4 Hz. Ir analysis in CCl_4 solution showed characteristic bands at 1750 (S), 1690 (S), 1670 (S), 1635 (W), 1260-1230 (S); broad doublet, 1080 (S), 855 (S). Mass spectral analysis gave M^+ at 182 and a fragmentation pattern consistent with the proposed structure. Anal. Calcd for $C_9H_{10}O_4$: C, 59.33; H, 5.53. Found: C, 58.99; H, 5.45.), (vii) unidentified component (trace, <2%). Difficulty was encountered in obtaining a sufficient quantity of this product, uncontaminated with **3**.

2. Electrolysis of Anisonitrile. In a similar manner as above, 1.3 g of anisonitrile was electrolyzed at 2.00 and at 2.50 V with passage of 1480 C. GC analysis showed only the presence of anisonitrile as well as some peaks in the low retention region corresponding to solvent oxidation products.

3. Electrolysis of 1,4-DMB in CH_3OH–Saturated KOCN. Using the H-cell and technique above a controlled potential electrolysis was carried out on 1,4-DMB (5.0 g, 0.036 mol) in saturated KOCN in CH_3OH solution using a Pt (10 cm^2) anode and a carbon rod cathode at 9°. The anolyte volume was 120 ml. The electrolysis potential was 1.50 V vs. SCE and after 6891 C (no. of electrons/1,4-DMB is thus 2.0) the initial current (410 mA) had dropped to zero. The anolyte was evaporated to dryness and the product taken up in anhydrous ether. This was filtered and the solvent was removed *in vacuo* leaving a solid which was identified as the quinone diketal (**2**) formed in 98% CE according to NMR analysis. The NMR and ir spectra of this product showed that the product was uncontaminated by possible cyanate or carbamate side-products.

A second controlled potential electrolysis of 1,4-DMB conducted under similar conditions but at 1.13 V gave the quinone diketal in about 100% CE.

References and Notes

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