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(12) Uv (CH_3CN) λ_{max} 251 (1.46×10^4), 377 sh (8.6×10^3), 397 sh (1.49×10^4), 420 (1.84×10^4); ir (KBr) (μm) 5.5 (w), 6.2 (w), 6.5 (s), 6.85 (m), 7.12 (w), 7.25 (s), 7.3 (s), 7.35 (s), 7.82 (m), 8.3 (w), 8.45 (s), 9.3 (m), 12.6 (s). Anal. Calcd for $C_{10}H_4S_4$: C, 47.62; H, 1.60; S, 50.78. Found: C, 47.65; H. 1.59.
(13) There is no need to discuss the two oxidation waves (0.55 (peak) and 0.93 V (peak), as suggested by a referee) because they are clean, fully reversible redox steps much like those found in simple inorganic systems (e.g., $Cu \rightleftarrows Cu^I \rightleftarrows Cu^{II}$, etc.). They are not encumbered by coproportionation or disproportionation problems since the radical cation is *indefinitely* stable in solution and can be *isolated*. However, the reduction wave (−1.14 V, peak) followed by reoxidation to TTN at −0.06 V (peak) deserves some explanation which should be deferred to the full paper on this subject.
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On the Sensitive Probe for Double Layer Structure. Potential Dependent Competitive Cyanation and Methoxylation of 1,4-Dimethoxybenzene

Sir:

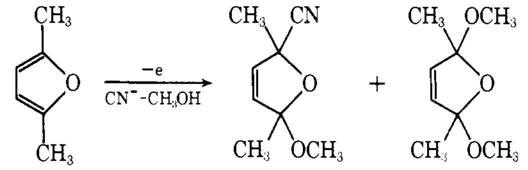
A recent paper by Weinberg et al.,[1] which deals with a competitive anodic cyanation and methoxylation, contains serious errors which cast considerable doubt upon their conclusions. They calculated the concentration of cyanide and methoxide ions using Ritchie's $K_b \simeq 10^{-3}$ *M* for cyanide,[2] however, overlooked the fact that the equilibrium constant did not contain the solvent term. Thus a 0.5 *M* NaCN-CH_3OH solution will actually contain approximately 0.48 *M* cyanide and 0.02 *M* methoxide ions. This shows that, if their assumptions are correct, the ratio of (CN^-/CH_3O^-) in the bulk of solution becomes greater than that at the electrode at the 1.3 V or less potential region (see Table II in ref 1). This is a queer result in view of both strong chemisorption of cyanide ion on platinum[3,4] and the independence of the product distribution on potential.[5] Even at as low a potential as 0.4 V, cyanation occurs efficiently.[6] In case II, the correct numerals cannot be used, since the value of **3y** would be greater than that of **3**.[7]

Table I. Relative Concentration of Cyanide and Methoxide Ions at Equilibrium in Methanol[a]

[NaCN], *M*	(CN^-/CH_3O^-)
0.1	9.5
0.5	21.7
1.6[b]	39.0

[a] $K_b \simeq 10^{-3}$ *M*, ref 2. [b] Saturated solution.

Scheme I



Previously we reported the competitive cyanation and methoxylation of 2,5-dimethylfuran.[5] A 2:1 isomeric mixture of *cis*- and *trans*-2-cyano-5-methoxy-2,5-dimethyldihydrofurans was formed together with small amounts of *cis*- and *trans*-2,5-dimethoxy-2,5-dimethyldihydrofurans. There was no variation in product distribution over a significant region of concentration (0.1–0.8 *M*). The product distribution was also unaltered with anode potential. These observations clearly show that nucleophiles are strongly adsorbed on the anode and do not vary markedly with the bulk concentration or potential. The analogous situation should also be maintained in the case of 1,4-DMB at the same material electrode. Thus the origin of apparent potential dependency of the current efficiencies of anisocyanide and the quinone diketal must be sought for elsewhere. One explanation may be that the cation radical of 1,4-DMB is not adsorbed as strongly as is that of 2,5-dimethylfuran, diffuses into the bulk solution which contains a greater relative concentration of methoxide ion, and consequently produces a greater part of the quinone diketal with the decreasing in sodium cyanide or with the lowering in anode potential. Table I shows the relation between the ratio of cyanide and methoxide ions at equilibrium and an initial concentration of sodium cyanide. It is apparent from the table that the relative concentration of methoxide ion increases with the decreasing of the initial concentration of sodium cyanide.

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.[1] If nucleophilic attack occurs in a heterogeneous environment (i.e., on the electrode), reaction will proceed stereospecifically. The cyanomethoxylation products of 2,5-dimethylfuran were, however, equilibrium mixtures of the cis and trans isomers.[5] In addition, the addition of substrate such as cyclohexene or toluene, which has a high oxidation potential, results in a remarkable decreasing of the current in the region 1.4–1.8 V. Substrate is strongly adsorbed on the anode to expel cyanide and methoxide ions. Hence we support their proposal, i.e., reaction of nucleophile with anodically produced cationic species occurs in the double layer.

References and Notes

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