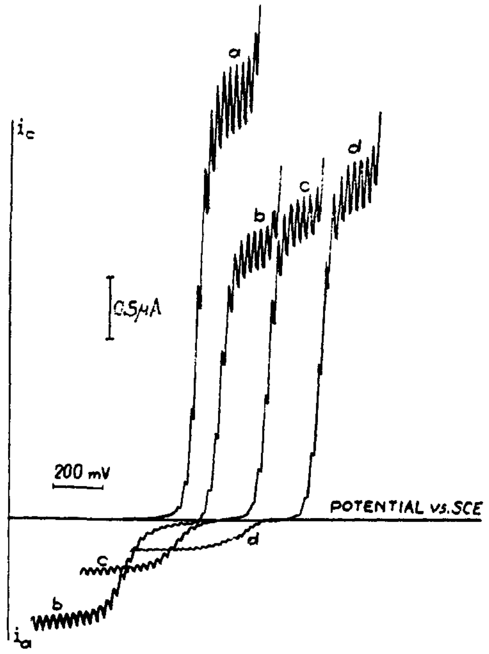

Figure 1. Polarographic curves of 1.3×10^{-3} *M* fluorenone in aqueous 38 vol % ethanol, 0.15 *M* NaOH, at 24°: (a) before electroreduction; (b) just after stopping a controlled-potential ($E = -1100 \pm 10$ mV *vs.* sce) electrolysis of 10-min duration; (c) 15 min later; (d) 30 min later. All curves begin at −0. 3V.

It is difficult to explain why Michielli and Elving could not observe the anodic wave of benzpinacol.[1] Most probably, benzpinacol was absent in their sample at the moment of recording a polarogram. Perhaps their "commercial benzpinacol, used as received,"[1] did not already contain the compound, or the pinacol decomposed in solution prior to the measurement. Benzpinacol is easily oxidized to benzophenone, undergoes dismutation (1) in the presence of traces of base, and isomerizes to benzopinacoline. It must be thoroughly checked before use and the solutions must be prepared with necessary precautions.

Our conclusions are further supported by recent results of Nekrasov and Korsun[7,8] who studied the reduction of aromatic ketones on a rotating disk–ring electrode and found the anodic waves of benzpinacol and fluorenopinacol oxidation. All available evidence, with the exception of the report of Michielli and Elving, confirms that aromatic pinacols oxidize at a mercury anode.

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Oxidation of Benzpinacol in Alkaline Solution

Sir:

In a study of the electrochemical reduction of benzophenone in pyridine,[1] the statement was made that the oxidation of benzpinacol to benzophenone at the dme in alkaline aqueous ethanol solution (0.12 *M* NaOH in 68% (v/v) EtOH), as reported by Kemula, *et al.*,[2] could not be duplicated; this was ascribed to chemical decomposition of the pinacol before it could be measured. This work has been repeated under conditions which minimize decomposition of the pinacol and the oxidation previously reported[2] has been observed.

Three samples of benzpinacol—prepared chemically, electrochemically, and photochemically—were examined in the solution composition indicated by direct current polarography (scan rate of 0.2 V/min) and an anodic wave was observed with $E_{1/2}$ of −0.60 V (−0.58 V previously reported[2]), which decreases with time while the benzophenone cathodic wave increases. The rate of decrease in height of the anodic wave increases markedly as the alkalinity increases.

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On Energy Localization of Approximate Molecular Orbitals[1]

Sir:

Energy-localized molecular orbitals (LMO's) obtained from the Edmiston–Ruedenberg (ER) method[2] are useful since they conform to intuitive ideas of chemical bonding. Applications of this method using semiempirical molecular orbitals are of particular interest since such MO's are at present readily available for a much wider range of molecules than are *ab initio* orbitals. Trindle and Sinanoğlu[3a] have recently applied the ER localization method to the CNDO/2[3b] molecular orbitals of several molecules; however, some of their results, especially for unsaturated systems, do not agree with the corresponding LMO's obtained from *ab initio* calculations.[4–6] In addition, it has been shown[7] that the fact that CNDO spherically averages electron-repulsion integrals can lead to an indeterminacy in the resulting LMO's. It is the purpose of this note to demonstrate that the less approximate INDO theory[8] is a more appropriate method to use for localization. Since INDO includes distinguishable one-center integrals, one would expect this method to give a more reasonable description of the atomic components of a molecule and thus of the canonical and localized orbitals as well.

(1) Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission. Contribution No. 2583.

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