

Letter

The Mechanism of the Deprotonation of Electrogenerated Cation Radicals of Methylarenes

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The deprotonations of the cation radicals of durene (DU), pentamethylbenzene (PMB) and hexamethylbenzene (HMB) generated electrochemically in acetonitrile follow rate law (1).

$$\text{Rate} = k_{\text{app}}[\text{ArCH}_3^{\cdot+}]^2 \quad (1)$$

This has now been established by both derivative cyclic voltammetry (DCV) and linear sweep voltammetry (LSV). The DCV reaction order analysis¹ of these reactions is illustrated by Fig. 1. The reaction order relationship which applies is (2) in which R_A , R_B , and R_I are the reaction orders in substrate, cation radical and any species generated in the reaction which further participates in controlling the rate, respectively.

$$R_{A/B(I)} = R_A + R_B + (R_I) = 1 + d \log v_{0.3} / d \log C_A \quad (2)$$

In (2) $v_{0.3}$ refers to the voltage sweep rate at which the derivative peak ratio during DCV was observed to be equal to 0.300. The slopes of the plots were observed to be equal to 1.01 (PMB), 0.90 (HMB) and 0.95 (DU) indicating that in all three cases $R_{A/B(I)}$ is very nearly

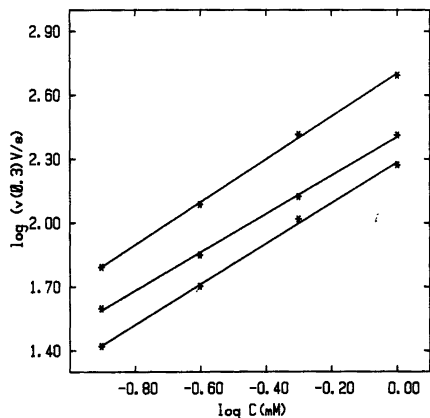


Fig. 1. Reaction order plots for the oxidation of PMB (upper line), HMB (center line) and DU (bottom line) in acetonitrile- Me_4NBF_4 (sat.) at 19.1 °C.

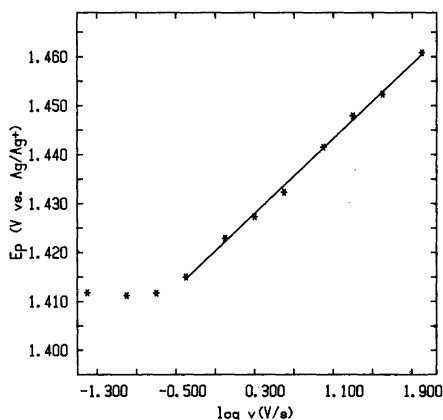


Fig. 2. Linear sweep voltammetry study of the oxidation of PMB (0.25 mM) in acetonitrile- Me_4NBF_4 (sat.) at 19.1 °C.

equal to 2.0. None of the three electrode processes are ideal, some adsorption was evident in the response.

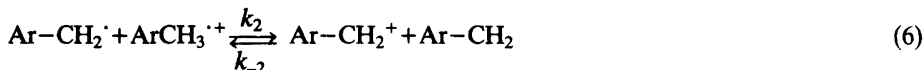
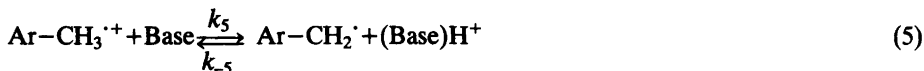
Further details of the reaction orders were obtained from LSV studies. A plot of E^P vs. $\log v$ obtained for the oxidation of PMB is shown in Fig. 2. The slope of the solid line (v ranging from 0.4 to 100 V/s) was observed to be equal to 19.1 mV/decade. The adsorption problem, which was noted in a previous study² is evident from the points at the lowest sweep rates (v equal to 0.04, 0.1 and 0.2 V/s). However, reliable results for both $dE^P/d \log v$ and $dE^P/d \log C_A$ could be obtained at sweep rates greater than 0.4 V/s. The reaction orders were derived from eqns. (3) and (4)³ along with experimental values of the two slopes.

$$dE^P/d \log v = \kappa / (R_B + 1) \quad (\kappa = (\ln 10)RT/F) \quad (3)$$

$$dE^P/d \log C_A = \kappa (R_A + R_B + (R_I) - 1) / (R_B + 1) \quad (4)$$

For all three compounds, $dE^P/d \log v$ and $dE^P/d \log C_A$ were within 1 mV of 19.3 mV, the theoretical value for $\kappa/3$ under the conditions of the experiments. These results are only consistent with $R_B = 2$ and $R_A = R_I = 0$.

These reactions have previously been discussed^{2,4-9} within the framework of mechanism (5)–(7) where the Base was not known.



The only circumstance under which this mechanism could be consistent with rate law (1) is if the reaction layer at the electrode is highly acidic and effectively buffered so that $(\text{Base})\text{H}^+$ is a constant and the reaction orders are unaffected by reverse reaction (5). The possibility of acidic layers close to anodes has been discussed earlier.¹⁰

Reversibility of reaction (5) was ruled out by conducting the DCV experiments with different rest potentials between scans. The height of the peak for the reduction of $\text{HMB}^{\cdot+}$ was observed to be very nearly independent of whether the electrode was held at +0.7 or -1.0 V (vs. Ag/Ag^+) between the scans. An acidic layer is possible when the electrode is held at positive potentials but at -1.0 V any excess protons in the reaction layer would undergo reduction.

A mechanism consistent with the kinetic data involves a reversible dimer formation (8) followed by rate determining proton transfer (9).



This mechanism accounts for the negative activation energy observed for the decomposition of $\text{HMB}^{\cdot+}$ as well as the primary kinetic isotope effect for experiments conducted with $\text{HMB}-d_{18}$. Thus, mechanism (5)–(7) appears to be ruled out under the conditions of this study and mechanism (8)–(9) is the most likely possibility. No other mechanism has been considered which accounts for all of the kinetic data.

There is no evidence for the nature of dimer²⁺. A definite possibility is that C–C bond formation is involved and that proton loss can take place as in (9) or from a ring position when these are unsubstituted to give biaryls. Biaryls and diphenylmethanes are often formed along with $\text{ArCH}_2\text{NHCOCH}_3$ which is the major product of oxidation in acetonitrile of the substrates used in this study.¹¹

Direct deprotonation of methylarene cation radicals apparently does take place during the metal ion oxidations.¹²⁻¹⁵ One might wonder how the two types of oxidations differ so

that two completely different mechanisms occur. The answer to this question is clear. During metal ion oxidations the cation radical concentrations are exceedingly small and second order reactions are precluded. If it were possible to study the electrochemical oxidations at comparable concentrations it is highly likely that mechanism (5)–(7) would indeed be observed under those conditions.

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