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Deprotonation of Methylarene Cation Radicals in Acetonitrile. An Unexpected Second-Order Mechanism

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Abstract: The kinetics of the deprotonation reactions of the cation radicals of several methylarenes were studied by derivative cyclic voltammetry (DCV) and derivative linear-sweep voltammetry (DLSV) in acetonitrile. The kinetic data indicate rate law i and suggest a mechanism consisting of reversible dimerization (reaction ii) followed by rate-determining deprotonation (reaction iii). Deuterium kinetic isotope effects were observed for the reactions of hexamethylbenzene (HMB) and HMB-d_{18}.

$$\text{rate} = k_{\text{app}}[\text{Ar-CH}_3^{\bullet+}]^2 \tag{i}$$

$$2\text{ArCH}_3^{\bullet+} \underset{k_{-ii}}{\overset{k_{ii}}{\rightleftharpoons}} \text{dimer(2+)} \tag{ii}$$

$$\text{dimer(2+)} + \text{B} \xrightarrow{k_{iii}} \text{ArCH}_2^+ + \text{ArCH}_3 + \text{BH}^+ \tag{iii}$$

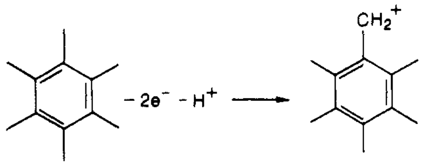
The value of k_H/k_D was observed to be 4.6 at 50 °C and to decrease monotonically with temperature to 1.5 at −30 °C. In the presence of trifluoroacetic acid (0.1%), k_H/k_D varied from 3.2 at +60 °C to approximately 1 at temperatures lower than −20 °C. In both solvent systems, Arrhenius plots were curved with approximately linear regions at either extreme of T. Above +20 °C, apparent E_a values of the order of −4.3 kcal/mol were observed. The changes in k_H/k_D and in apparent E_a with temperature are consistent with the mechanism (ii) + (iii) with k_{app} equal to k_{ii} at one limit (low T) and to $k_{iii}K_{ii}$ at the other (high T). At the low-T limit the deuterium kinetic isotope effect is predicted by this mechanism to disappear, and the activation energy should then reflect only the forward reaction (reaction iii). In the transition region between the limiting cases, k_{app} is equal to $k_{ii}k_{iii}/(k_{-ii} + k_{iii})$, which gives rise to the observed dependences of E_a and k_H/k_D upon the temperature. The mechanism of the reaction is discussed in relation to other cases where negative activation energies and temperature-dependent kinetic isotope effects are observed.

Proton transfer from cationic intermediates is of great importance during the oxidation of organic compounds. In most cases the oxidation reactions involve several coupled steps, and it is difficult to isolate particular steps, for example, the reaction of the positively charged intermediate with a base, for detailed studies.

The deprotonation of methylarene cation radicals, formed by oxidative electron transfer, is a class of reactions of this type which are possible to study in detail. The reaction kinetics have been studied during metal-ion oxidation,[1-5] by pulse radiolysis,[6] and by electrochemical techniques.[7-14]

During the oxidation of methylarenes such as toluene, studies of the proton-transfer reaction are complicated by competing nucleophilic attack and coupling reactions. For this reason highly substituted methylarenes, particularly hexamethylbenzene (HMB), have been widely used as substrates for oxidation studies. In the case of HMB there are no unsubstituted ring positions to invite competing reactions.

The anodic oxidation of HMB in acetonitrile results in the generation of the corresponding benzyl cation (eq 1), which is attacked by solvent and water to form the acetamide derivative (eq 2).[15,16] The early studies of this reaction left little doubt that the process involves the benzylic cation as an intermediate but did not provide much evidence for the detailed reaction pathway. Voltammetric and spectroelectrochemical studies provided a wealth of new detail on the reaction pathway using HMB and a number of other methylarenes (ArCH_3) as substrates.[7-11] These studies resulted in the observation of cation radicals ($\text{ArCH}_3^{\bullet+}$), benzyl radicals ($\text{ArCH}_2^\bullet$), benzyl cations (ArCH_2^+), and even benzylnitrilium ions ($\text{ArCH}_2\text{N{=}C}^+\text{CH}_3$) as reaction intermediates.



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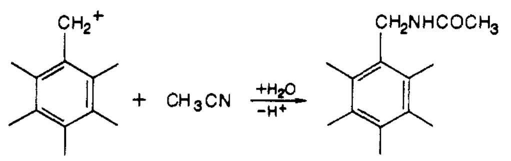

(2)

The mechanistic studies resulted in the proposal that essentially irreversible reactions 3–5 resulted in the formation of the nitrilium ions.[7-11]

$$\text{ArCH}_3^{\bullet+} + \text{B} \underset{(k_{-3})}{\overset{k_3}{\rightleftharpoons}} \text{ArCH}_2^\bullet + \text{BH}^+ \tag{3}$$

$$\text{ArCH}_2^\bullet + \text{ArCH}_3^{\bullet+} \underset{(k_{-4})}{\overset{k_4}{\rightleftharpoons}} \text{ArCH}_2^+ + \text{ArCH}_3 \tag{4}$$

$$\text{ArCH}_2^+ + \text{CH}_3\text{CN} \xrightarrow{k_5} \text{ArCH}_2\text{N{=}C}^+\text{CH}_3 \tag{5}$$

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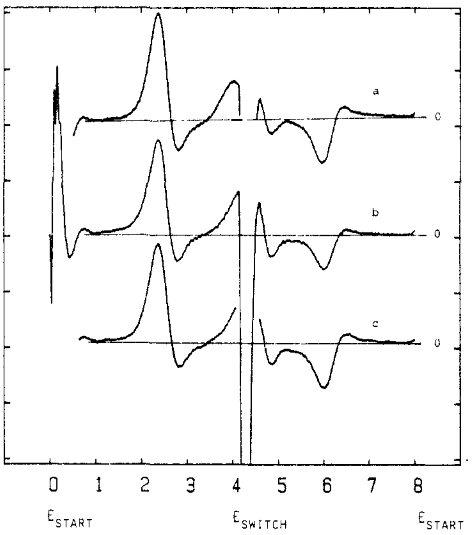

Figure 1. Derivative cyclic voltammograms for the oxidation of methylarenes in acetonitrile at 100 V/s. (a) HMB (0.25 mM) $E_{\text{start}} = +0.84$ V. (b) PMB (0.25 mM) $E_{\text{start}} = +0.94$ V. (c) DU (0.25 mM) $E_{\text{start}} = +1.02$ V. In the presence of Me_4NBF_4 (0.05 M) at 19 °C.

Later, a linear-sweep voltammetry study indicated that the reaction order in $ArCH_3^{\bullet+}$ was 2, and to be consistent with this reaction scheme, reaction 3 was suggested to be reversible under the reaction conditions and reaction 4 was implicated in the reaction kinetics.[12] A derivative cyclic voltammetry (DCV) study also showed a reaction order in cation radical of >1 and supported the conclusion that reaction 3 must be considered reversible in order to account for the kinetics.

The nature of B in reaction 3 is uncertain in the absence of added base. The pK_a values estimated for toluene (−12)[17a] and hexamethylbenzene (+1)[17b] cation radicals in acetonitrile would appear to support the possibility of reversible proton transfer to acetonitrile (pK_a of $CH_3C^+{=}NH = -10$). However, acetonitrile solutions invariably contain a much stronger base, water (pK_a of $H_3O^+ = 1.8$), unless extreme precautions are taken to keep reaction mixtures dry. This, along with the fact that some of the kinetic data[12] would appear to require reaction 4 to be reversible as well, casts serious doubt on the validity of this mechanism under all circumstances. The oxidation potential of the benzyl radical has been estimated to be about 1.1 V less anodic than that for toluene.[18] This suggests that the equilibrium constant for reaction 4 is probably of the order of 10^{18}. Thus, reaction 4 cannot be considered to be reversible when followed by irreversible reaction 5.

Soon after this investigation was begun, it became apparent that the kinetic data cannot be accounted for within the framework of reactions 3–5.[14] In this paper the evidence for a radically different mechanism is presented. HMB and HMB-d_{18} were studied most extensively, but two other highly substituted methylarenes, pentamethylbenzene (PMB) and symmetrical tetramethylbenzene (durene = DU), were included to show some generality of the mechanism.

Results

Derivative Cyclic Voltammetry of Methylarene Oxidations. The DCV analyses of these reactions were carried out by using procedures described earlier.[19-21] Voltammograms for the three substrates, HMB, PMB, and DU, are illustrated in Figure 1. The scans were obtained at 100 V/s on substrate solutions (0.25 mM) in $MeCN-Me_4NBF_4$ (0.05 M). The starting potentials were adjusted so that the switching potential (E_{switch}) was 300 mV positive of the reversible potentials for the processes. The parameter measured for the kinetic analyses was R_I' defined as the ratio of the peak heights on the reverse and forward scans measured from the zero lines indicated in the figure. In practice the data are analyzed directly by using an on-line computer rather than from the recordings which are included only for illustration of the method.

Table I. Reaction-Order Data for the Decomposition Reactions of Methylarene Cation Radicals in Acetonitrile[a]

C_A,[b] mM	$\nu_{0.3}$, V/s DU	HMB	PMB
0.125	26.3	39.6	61.9
0.250	50.3	70.4	122
0.500	104	133	260
1.000	187	258	493
R_B[c]	1.95	1.90	2.00

[a] Measurements by derivative cyclic voltammetry at a platinum electrode at 292.2 K in solvent containing Me_4NBF_4 (0.07 M). [b] Substrate concentration. [c] Reaction order in cation radical.

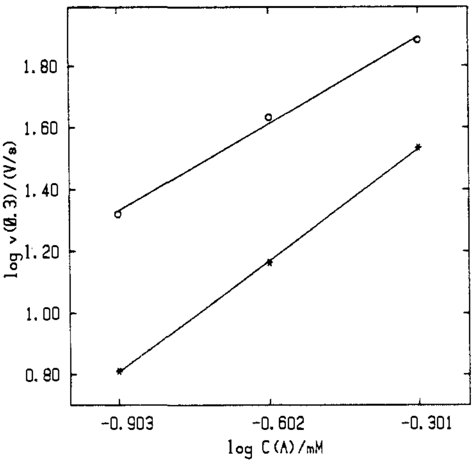

Figure 2. Reaction-order plots for methylarene cation radical deprotonation in $MeCN-Bu_4NBF_4$ (0.1 M) at −41 °C, (O) HMB and (*) HMB-d_{18}.

DCV Reaction-Order Analyses. The DCV reaction-order relationship[22] applicable to the study of these reactions is eq 6. The overall reaction order, $R_{A/B(I)}$, includes contributions from the electrode-generated intermediate (R_B), possibly from the substrate (R_A) and possibly from species generated during the reaction (R_I) which contribute to the rate. The latter contribution is enclosed

$$R_{A/B(I)} = R_A + R_B + (R_I) = 1 + d(\log \nu_c)/d(\log C_A) \quad (6)$$

in parentheses to emphasize that it is usually 0. The value of $R_{A/B(I)}$ is obtained as 1 plus the slope of a plot of log ν_c vs. log C_A, where ν_c is the voltage sweep rate necessary to obtain R_I' equal to c and C_A is the substrate concentration. Data for the three substrates are given in Table I. In this case ν_c is $\nu_{0.3}$, i.e., the sweep rate necessary for R_I' to equal 0.300. Data were obtained with C_A ranging from 0.125 to 1.00 mM with reaction orders all very near 2.0. These are given as R_B, i.e., R_A and R_I equal to 0, to be compatible with derivative linear-sweep voltammetry (DLSV) data discussed later. The plots of these data were shown in the preliminary communication of this work.[14]

Since kinetic data were gathered over a very wide temperature range, it was necessary to determine whether or not the reaction orders are affected by the temperature. The plots shown in Figure 2 are for the reactions of the cation radicals of HMB and HMB-d_{18} at −41 °C. Reaction orders of 1.94 and 2.20, respectively, were observed for these reactants. The plot in Figure 3 is for the oxidation of HMB-d_{18} at 60 °C which resulted in a slope of 1.09 and R_B equal to 2.09. Thus, it appears that the reaction orders

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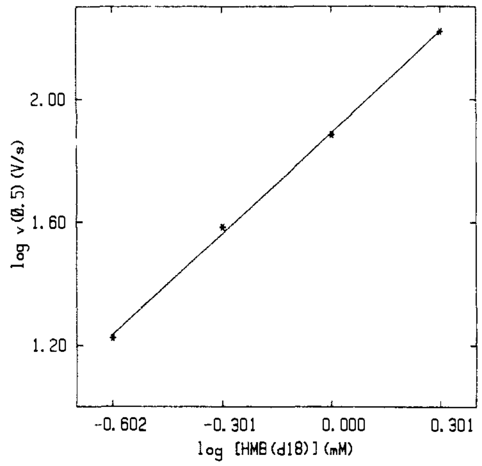

Figure 3. Reaction-order plot for the deprotonation of HMB-d_{18} at 60 °C in MeCN–Me_4NBF_4 (0.05 M).

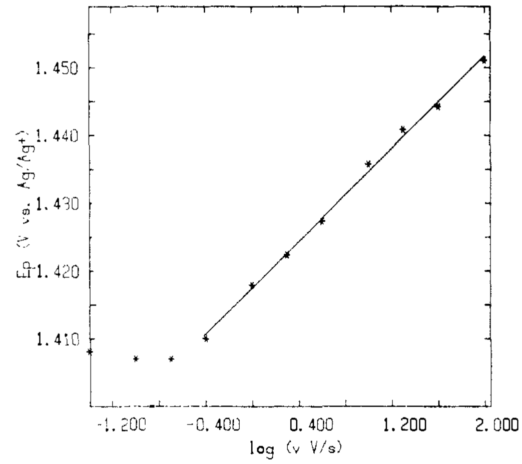

Figure 4. Linear-sweep voltammetry peak potentials as a function of sweep rate for the oxidation of PMB (0.25 mM) in MeCN–Me_4NBF_4 (0.05 M) at 19 °C.

observed by DCV are very close to 2 and independent of temperature. All experiments were carried out in MeCN–$Me_4N^+BF_4^-$ (0.05 M).

DLSV Reaction-Order Analysis. Linear-sweep voltammetry reaction-order studies have a definite advantage over those from the direct electrochemical techniques such as DCV. The advantage is that the reaction orders in substrate (R_A) and intermediate (R_B) are separated in LSV studies. The reaction orders are obtained from the slopes $dE_p/d \log \nu$ and $dE_p/d \log C_A$ by eq 7 and 8 in which $\kappa = (\ln 10)RT/F$.[23] These equations hold for reactions in which the reaction orders do not change with concentration.[24]

$$dE_p/d \log \nu = \kappa(R_B + 1)^{-1} \qquad (7)$$

$$dE_p/d \log C_A = \kappa(R_A + R_B + R_I - 1)(R_B + 1)^{-1} \qquad (8)$$

Some difficulty with product adsorption was encountered in an earlier DLSV study of methylarene oxidation in acetonitrile.[12] These problems can be minimized by avoiding sweep rates less than 400 mV/s. This is demonstrated by the data in Figure 4. The solid line is for sweep rates between 0.4 and 100 V/s. The slope of this line, $dE_p/d \log \nu$, is equal to 19.1 mV/decade, which corresponds to $R_B = 2$ from relationship 7. The point of interest here is that the data at lower sweep rates, 50–200 mV/s, are nearly independent of ν. At these sweep rates the peak potentials obtained depended very much on how the electrode was treated, i.e., cleaned between scans or not, as is usual when adsorption is a problem.

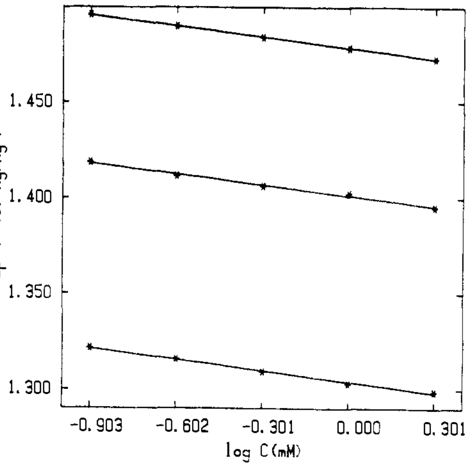

Figure 5. Linear-sweep voltammetry peak potentials for the oxidation of methylarenes in MeCN–Me_4NBF_4 (0.05 M) as a function of substrate concentration at 19 °C and 400 mV/s. The plots from top to bottom refer to DU, PMB, and HMB, respectively.

Table II. Linear-Sweep-Voltammetry Kinetic Data for the Oxidation of Hexamethylbenzene in Acetonitrile[a]

C_{HMB}, mM	$\Delta E_p/\Delta$ log ν[b]	$\Delta E_p/\Delta$ log C_A[c]	$\Delta E_p/\Delta$ log C_A[d]
0.25	19.3 (0.5)		
		20.6 (0.9)	19.8 (0.2)
0.50	19.9 (0.1)		
		20.1 (0.4)	21.1 (0.6)
1.00	19.5 (0.3)		
		19.5 (0.7)	19.1 (0.7)
2.00	19.3 (0.4)		
		17.1 (0.7)	19.3 (1.2)
4.00	18.3 (0.7)		
	19.3 (0.6)[e]	19.3 (1.5)[e]	19.6 (1.0)[e]

[a] For measurements at a platinum electrode in solvent containing Me_4NBF_4 (0.07 M) at 291.9 K. [b] In mV/decade for measurements at 400 and 1000 mV/s. [c] In mV/decade for measurements at 400 mV/s. [d] In mV/decade for measurements at 1000 mV/s. [e] Mean value.

It is also expected that adsorption should be most problematic at low sweep rates since the electrode is active for longer times. Although the plot is linear to 100 V/s, data at high sweep rates can be questionable due to the possible interference of charge-transfer kinetics and the fact that the reaction is not fast enough to be suitable for DLSV analysis at the high sweep rates. These two factors influence the data in opposite directions so that data obtained at high sweep rates may appear to fit a particular relationship but for the wrong reason. More detailed studies were carried out at sweep rates between 0.400 and 1.00 V/s for the oxidation of HMB. The results are summarized in Table II. The theoretical value of $dE_p/d \log \nu$ for $R_B = 2.0$ is 19.3 mV/decade at 292 K. The value observed was 19.3 ± 0.6 mV/decade with substrate concentrations ranging from 0.25 to 4.0 mM. Mean values of $dE_p/d \log C_A$ of 19.3 ± 1.5 and 19.6 ± 1.0 mV/decade at 0.40 and 1.00 V/s, respectively, were observed. Plots of E_p vs. log C_A for PMB, HMB, and DU are shown in Figure 5. These resulted in $dE_p/d \log C_A$ equal to 18.6, 19.3, and 18.7 mV/decade at ν equal to 0.400 V/s.

The DLSV data are only consistent with eq 7 and 8 when R_B is 2.0 and R_A (as well as R_I) is 0.

Effect of Water on the Cation Radical Reaction Rates. The effect of water on the apparent rate constants for the decomposition reactions of the methylarene cation radicals in acetonitrile has a strong bearing on the question of the reversibility of reaction 3 as discussed earlier. Data for the effect of water on $\nu_{0.3}$ for the three substrates are summarized in Table III. The solutions with zero water added are from freshly distilled acetonitrile and dried Me_4NBF_4 prepared under nitrogen. The water content in these solutions was estimated to be of the order of 10 mM. Adding water to these solutions brought about small decreases in $\nu_{0.3}$ with

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Table III. Effect of Water on the Rate of Decomposition of Methylarene Cation Radicals in Acetonitrile[a]

substrate	$\nu_{0.3}$ at $[H_2O]_{added}$,[b] V/s		
	0	69.5	139
DU (0.25 mM)	44.8	48.6	59.0
HMB (0.25 mM)	70.0	68.0	65.7
PMB (0.25 mM)	124.5	116.3	117.9

[a] For conditions, see Table I. [b] $[H_2O]$ in mM.

Table IV. Effect of the Electrode Rest Potential on the Reduction Current for Hexamethylbenzene Cation Radical[a]

E_{rest},[b] V	t at E_{rest},[c] s	E_{start},[d] V	R_1'[e]	$(I_b')_{rel}$[f]
+0.74	30	+0.74	0.415	1.00
−1.00	20	+0.74	0.474	0.90
−1.00	25	+0.74	0.495	0.86
+0.74	60	+0.74	0.423	1.02
−1.00	55	+0.74	0.498	0.90

[a] For conditions, see Table I. [b] The potential at which the working electrode was held between DCV scans. [c] The time at the rest potential before stepping to E_{start} in seconds. [d] The potential from which the DCV scans started. [e] The DCV derivative peak ratio. [f] The relative height of the reduction peak due to HMB^+.

HMB and PMB and a small increase in the same with DU. This more or less rules out the participation of reverse reaction 3 in the kinetics in homogeneous solution.

Search for Evidence for an Acidic Region Near the Electrode. The reversibility of reaction 3 in the conventional sense was ruled out by the data in the previous section. Reverse reaction 3 could possibly affect the kinetics if the reaction layer at the electrode is highly acidic and effectively buffered. The possibility of acid layers close to the anodes has been discussed.[25] Although this possibility was not considered to be likely in this case, it was necessary to test for it. This was accomplished by carrying out DCV scans from different rest potentials. It was reasoned that at a rest potential of +0.74 V an acid layer could possibly exist but could not with the electrode held at −1.00 V between scans. The data in Table IV show that R_1' was observed to be slightly lower with E_{rest} equal to +0.74 V than when it was −1.00 V. The effect was relatively small, and no efforts were made to investigate it further. The point of importance with respect to the reversibility of reaction 3 is that a dramatic effect in the opposite direction is called for if an acidic layer contributes to the kinetics. Since this was not found, it would appear that any mechanism requiring reverse reaction 3 to participate is ruled out by the data.

Effect of Temperature on the Apparent Rate Constants for the Reactions of HMB Cation Radicals. The effect of temperature on $\nu_{0.3}$ for the reactions of the cation radicals of HMB in $MeCN-Me_4NBF_4$ (0.05 M) and in the same solvent to which trifluoroacetic acid, TFA (0.1% by volume), was added is illustrated by the plots shown in Figure 6 for the reactions carried out in the temperature range −40 to +60 °C. Addition of TFA was observed to improve the quality of the electrode response, especially at low temperatures, without affecting the form of the rate law (adsorption was so severe at −40 °C in the absence of TFA that $\nu_{0.3}$ could not be determined, and $\nu_{0.3}$ at −30 °C is highly uncertain). The plots of log (ν_c/T) vs. $1/T$ may be regarded as an Arrhenius relationship since ν_c is an apparent rate constant.[26] Curvature is apparent in both plots, indicating a change in the degree of influence of rate-determining steps with temperature. With added TFA the plot appears to be linear, within experimental error, at both extremes of temperature with apparent activation energies of +1.3 and −4.3 kcal/mol at the low and high extremities, respectively. The same trends, but less marked, appear in the absence of TFA but are obscured by experimental difficulties at low T. To test for linearity in the absence of TFA at the high extreme of T, more detailed studies were carried out between +40 and +60 °C at 5-deg intervals. Arrhenius plots for HMB and HMB-d_{18} are shown in Figure 7 for this temperature interval. The plots are linear within experimental error and yield an apparent E_a of −4.4 and −4.5 kcal/mol for HMB and HMB-d_{18} cation radicals, respectively. Results for four independent determinations of E_a for HMB in this temperature range are summarized in Table V. The data are linear within experimental error and give rise to a mean value of −4.3 kcal/mol with a standard deviation of ±0.3 kcal/mol.

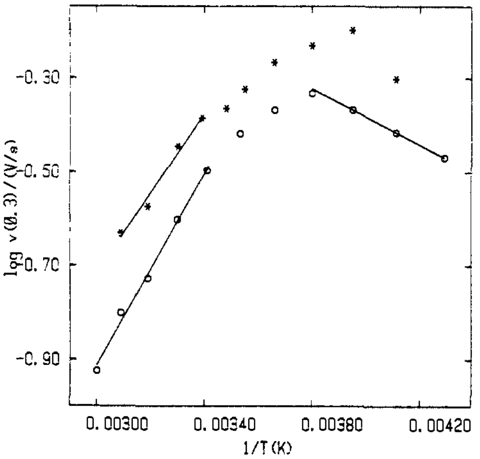

Figure 6. Effect of temperature on the apparent rate constants for the deprotonation of HMB cation radicals in $MeCN-Me_4NBF_4$ (0.05 M), (*) neutral solvent and (○) in the presence of TFA (0.1% by volume). The differences in reversible and switching potentials were 200 (neutral solvent) and 300 mV (in the presence of TFA).

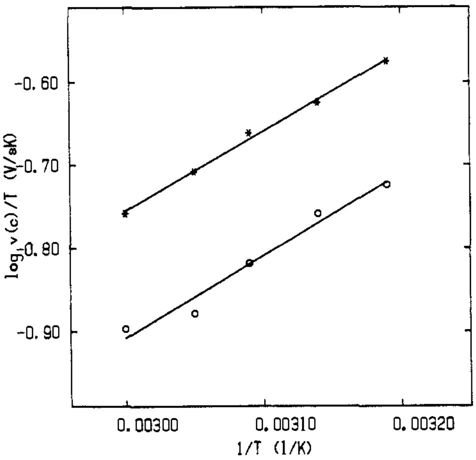

Figure 7. Arrhenius plots for the deprotonation of methylarene cation radicals, (*) HMB $\nu_{0.3}$ values, (○) HMB-d_{18} $\nu_{0.4}$ values in $MeCN-Me_4NBF_4$ (0.05 M).

Table V. Apparent Activation Energies for the Reaction of HMB Cation Radical in Acetonitrile[a]

run	E_a, kcal/mol	r[b]
1	−4.4[c]	0.987[c]
2	−4.6	0.994
3	−3.9	0.996
4	−4.3	0.994
	−4.3 ± 0.3	

[a] In solvent containing Me_4NBF_4 (0.05 M) with measurements at +40, +45, +50, +55, and +60 °C. Substrate concentration equal to 1.00 mM. [b] The linear-regression correlation coefficient. [c] The plot is shown in Figure 7.

Deuterium Kinetic Isotope Effects. Apparent rate constants $(\nu_{0.3}/T)$ were evaluated for the reactions of the cation radicals of both HMB and HMB-d_{18} over the entire accessible temperature range in both solvent systems. The apparent k_H/k_D values in neutral solvent and that to which TFA (0.1%) was added are summarized in Table VI. No effect on apparent rate constants was observed in the presence of TFA up to as much as 1% by

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Table VI. Deuterium Kinetic Isotope Effects for the Reactions of Hexamethylbenzene Cation Radical in Acetonitrile[a]

	$(k_H/k_D)_{app}$	
T, °C	neutral[b]	0.1% TFA[b]
+60		3.2
+50	4.6	2.8
+40	3.8	2.2
+30	3.2	2.2
+20	2.8 (+21.8)[c]	2.0
+10	2.3 (+8.8)[c]	1.9
0	2.1	2.0
-10	1.9	1.9
-20	1.8	1.2
-30	1.5	1.0
-40		1.2

[a] In solvent containing HMB (1.0 mM) and Me_4NBF_4 (0.05 M). [b] Neutral refers to the solvent in the absence of TFA, and 0.1% is the volume percent of TFA added. [c] Note the temperatures in these cases.

volume. In neutral solvent k_H/k_D decreases monotonically with temperature from 4.6 at the higher limit to 1.5 at the lower limit. In the TFA-containing solvent the trend was similar with limiting values of 3.2 and 1.2.

Calculation of Rate Constants for the Cation Radical Reactions. Up to now, we have not invoked any theoretical model to which to compare data with. The approach used, called the reaction-order approach,[21] involves determining the rate law directly from experimental data without implicating any particular theoretical model or reaction mechanism. From the rate law, along with the stoichiometric relationships, reaction mechanisms consistent with the data can be formulated. The rate law obtained by this approach in the present case is (9). The electrode reaction involves

$$-d[ArCH_3^{\bullet+}]/dt = k_{app}[ArCH_3^{\bullet+}]^2 \qquad (9)$$

the consumption of 2 faradays/mol to produce $ArCH_2$–$NHCOCH_3$ which leads to the stoichiometric eq 10. The rate law and the stoichiometry are then the total information that can be obtained from the electrode measurements, aside from kinetic isotope effects and activation energies, in cases where intermediates cannot

$$2ArCH_3^{\bullet+} + CH_3CN + H_2O \rightarrow ArCH_3 + ArCH_2\text{–}NHCOCH_3 + 2H^+ \qquad (10)$$

be detected. From this information the mechanism can be formulated in a form suitable to use to carry out theoretical calculations of the electrode response. The information available for the mechanism of the deprotonation of $ArCH_3^{\bullet+}$ under the conditions used in this study allows the mechanism to be written as eq 11 and 12. In eq 11 and 12 $ArCH_3$ is written in parentheses

$$2ArCH_3^{\bullet+} \xrightarrow{k_{app}} \text{intermediate} + (ArCH_3) \qquad (11)$$

$$\text{intermediate} + CH_3CN + H_2O \rightarrow ArCH_2\text{–}NHCOCH_3 + (ArCH_3) \qquad (12)$$

to emphasize that it is not known in what step the substrate is regenerated. This is admittedly a crude mechanism, and it is treated in this way here as a reminder that electrode-mechanism analysis, whether it be by the reaction-order approach or by the use of theoretical working curves, does not provide a reaction mechanism but gives a kinetic model which may fit a number of different detailed mechanisms. This fact is not always appreciated.

For the purpose of evaluating rate constants, k_{app} in this case, mechanism (11) + (12) is in the form needed. Calculations were carried out by digital simulation[27] for an irreversible second-order reaction regenerating substrate. The integrated form of the rate law was used in the simulation as had been recommended some time ago.[28,29] The theoretical data, along with experimental data for all three substrates, are summarized in Table VII. Data were evaluated for R_1' ranging from 0.300 to 0.600 at 0.050 intervals. Indications of how good the experimental and theoretical data compare are given by (i) the standard deviations in the calculated rate constants (shown in parentheses) and (ii) by whether or not there are trends in the calculated rate constants. Standard deviations were found to be of the order of ±6% or less, and there are no trends obvious in the data for any of the substrates. Therefore, it must be concluded that the experimental data give an excellent fit to kinetic model (11) + (12), and the rate constants observed, 1.65×10^7 to 3.46×10^7 M^{-1} s^{-1}, refer to k_{app} for reaction 11. Any further refinements that we can make of this mechanism will have to deal with the way in which k_{app} is defined. The additional evidence which can be used to refine the mechanism include the kinetic isotope effect and the activation energy data.

Table VII. Rate Constants Calculated by Relating Experimental DCV Data to Theoretical Data for a Second-Order Mechanism

	$k(RT/F)C_A/$	$10^{-7}k$, M^{-1} s^{-1} [b]		
R_1'	ν[a]	DU	HMB	PMB
0.300	1.809	1.51	2.28	3.51
0.350	1.166	1.61	2.19	3.40
0.400	0.798	1.69	2.05	3.34
0.450	0.562	1.63	1.96	3.48
0.500	0.402	1.64	2.01	3.59
0.550	0.289	1.80	2.15	
0.600	0.208		2.23	
		1.65 (0.10)[c]	2.12 (0.12)[c]	3.46 (0.10)[c]

[a] Theoretical data obtained by digital simulation as described in the text, refers to $E_{switch} - E_{rev}$ equal to 300 mV. [b] Conditions as in Table I with C_A equal to 0.125 mM in all cases. [c] Mean values.

Product Studies. To test for a possible effect of temperature on the course of the reaction, product studies were carried out at +50, +20, 0, and -40 °C. Electrolyses were carried out to about 50% conversion in the TFA-containing solutions, and after workup the reaction mixtures were analyzed by GLC. The only product detected was the corresponding acetamide, and the apparent yield was not dependent upon the temperature at which the electrolysis was carried out.

Discussion

Kinetic and Mechanistic Evidence. The results summarized in the previous sections show beyond any doubt that the deprotonations of the cation radicals of HMB, PMB, and DU do not take place by a simple proton transfer directly from the cation radicals. These results pertain to reactions of the cation radicals generated electrochemically in acetonitrile at temperatures ranging from -50 to +60 °C.

The evidence which is available for the formulation of a detailed mechanism can be summarized by the following: (i) The deprotonations follow a second-order rate equation (eq 9). (ii) Arrhenius plots of the apparent rate constants are curved with approximately linear segments at the temperature extremes indicating a complex expression for k_{app} and apparent negative activation energies at the high-T limit. (iii) The deuterium kinetic isotope effect, $(k_H/k_D)_{app}$, is dependent on the temperature increasing smoothly from close to unity at -40 °C to 3.2–4.6 at +50 °C. (iv) The observed second-order rate constants are large, $>10^7$ M^{-1} s^{-1}. (v) The apparent rate constants are very nearly independent of water concentration in the range studied (up to 140 mM).

Possibility of a Disproportionation Mechanism. The rate law, eq 9, as well as the stoichiometry of the reaction can be accounted for by a disproportionation mechanism consisting of rate-determining electron-transfer reaction (eq 13) followed by deprotonation of the dication (eq 14). However, the mechanism is inconsistent

$$2ArCH_3^{\bullet+} \underset{k_{-13}}{\overset{k_{13}}{\rightleftharpoons}} ArCH_3^{2+} + ArCH_3 \qquad (13)$$

$$ArCH_3^{2+} \xrightarrow{k_{14}} ArCH_2^{+} + H^+ \qquad (14)$$

with practically all of the other evidence. A deuterium kinetic

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isotope effect is not expected for the rate-determining electron-transfer reaction (eq 13). The apparent negative activation energies likewise cannot be accounted for by this mechanism. Furthermore, the observed rate constants are far too great to be consistent with this mechanism. The electrode potentials for the formation of the dications were not determined because of interfering processes due to reaction products, but based on results from related work,[30] it would appear safe to predict 500 mV to be a minimum potential difference for the formation of the cation radicals and the dications of the methylarenes. This leads to a maximum value of about 10^{-8} for the equilibrium constant for reaction 13. Following an analysis used earlier for a similar case[31] leads to a maximum possible rate constant for (13) of the order of 10^2 $\mathrm{M^{-1}\ s^{-1}}$, i.e., about 5 orders of magnitude lower than those observed in this study. These arguments clearly rule out the disproportionation mechanism for the deprotonation reactions of the methylarene cation radicals.

Deprotonation of Dimer Dications. A Reaction Mechanism Consistent with the Data. A mechanism consistent with all the data and chemical considerations involves the reversible formation of a dimer dication (eq 15) followed by a dissociative deprotonation (eq 16) to the benzyl cation which goes on to products. Invoking

$$2\mathrm{ArCH_3}^{\bullet+} \underset{k_{-15}}{\overset{k_{15}}{\rightleftharpoons}} \mathrm{dimer(2+)} \tag{15}$$

$$\mathrm{dimer(2+)} + \mathrm{B} \xrightarrow{k_{16}} \mathrm{ArCH_2}^+ + \mathrm{ArCH_3} + \mathrm{BH}^+ \tag{16}$$

the steady-state approximation on [dimer(2+)] results in rate law (17).

$$-d[\mathrm{ArCH_3}^{\bullet+}]/dt = 2(k_{15}k_{16}/(k_{-15} + k_{16}[\mathrm{B}]))[\mathrm{ArCH_3}^{\bullet+}]^2[\mathrm{B}] \tag{17}$$

In the following, each point of evidence is discussed in relation to mechanism (15) + (16).

(i) This mechanism predicts that the reaction order in cation radical will be 2 under all circumstances. The only quantity that changes with changes in the conditions is k_{app}, which is equal to $2(k_{15}k_{16}/(k_{-15} + k_{16}[\mathrm{B}]))$, contains only rate constants and a term for the concentration of base which is in excess, and remains unchanged during an experiment. This is precisely the type of complex mechanism where the complexity is not manifested in the electrode response[22] and must be detected by other means. Since the experimental data were used to derive rate law 9, which is equivalent to (17), the electrochemical kinetics support this mechanism.

(ii) Rate law 17 predicts two limiting cases depending upon the relative values of the terms in the denominator. In the first case, $k_{-15} \gg k_{16}[\mathrm{B}]$ and the rate law becomes (18). The activation energy corresponding to rate law 18 consists of two terms, $\Delta H°$

$$-d[\mathrm{ArCH_3}^{\bullet+}]/dt = 2k_{16}K_{15}[\mathrm{ArCH_3}^{\bullet+}]^2[\mathrm{B}] \tag{18}$$

for reaction 15 and E_a for reaction 16. Since $\Delta H°$ for the monomer–dimer equilibrium can assume rather large negative values, the positive E_a for (16) is masked, and the observed E_a can have appreciable negative values. There have been a number of such cases reported.[32-45] The interpretation is very nearly the same in all cases; a reactive intermediate is formed in preequilibrium with a negative $\Delta H°$ which causes the apparent E_a to be very small or have negative values. Some of these cases are listed in Table VIII.

Table VIII. Examples of Reactions with Low or Negative Activation Energies Passing through a Preequilibrium

reaction type	ref
dimerization of phenoxy radicals	32–35
proton transfer to tertiary amines	36
photochemical reactions	38–41
Diels–Alder reaction	41
reaction of methylphenylketene	42
dimerization of 9-substituted anthracene anion radicals	43
dimerization of diethyl fumarate anion radicals	44
dimerization of sulfur dioxide anion radical	45

At the other limit, $k_{-15} \ll k_{16}[\mathrm{B}]$, rate law 19 is valid and E_a is predicted to be normal and positive. The results do indeed suggest that at the lowest temperatures (Figure 6) the apparent

$$-d[\mathrm{ArCH_3}^{\bullet+}]/dt = 2k_{15}[\mathrm{ArCH_3}^{\bullet+}]^2 \tag{19}$$

rate constant does begin to decrease with decreasing temperature to give an apparent positive E_a as predicted. The results are clearly those expected for mechanism (15) + (16) in the transition region between limiting cases where rate law 17 is applicable.

(iii) Mechanism (15) + (16) predicts a range of $(k_{\mathrm{H}}/k_{\mathrm{D}})_{\mathrm{app}}$ as was observed. At the low-T limit where rate law 19 would apply, there should be no deuterium kinetic isotope effect. In fact, $(k_{\mathrm{H}}/k_{\mathrm{D}})_{\mathrm{app}}$ does decrease with temperature and appears to be approaching 1 at the lowest T. At the high-T limit where rate law 18 is expected, the deuterium kinetic isotope effect for the proton-transfer reaction (eq 16) should be fully apparent. The value observed at +50 °C, $(k_{\mathrm{H}}/k_{\mathrm{D}})_{\mathrm{app}} = 4.6$, in the absence of TFA appears to be very similar to that observed in a reaction with some similar features, i.e., the attack of base on the benzylic C–H(D) during elimination reaction 20.[46]

$$\mathrm{PhCD_2CH_2N^+Me_3} + \mathrm{OH^-} \rightarrow \mathrm{PhCD{=}CH_2} + \mathrm{H_2O} + \mathrm{Me_3N} \tag{20}$$

(iv) The large second-order rate constants observed can also be accounted for within the framework of mechanism (15) + (16). The derivation of rate law 17 assumes that the equilibrium constant for reaction 15 is about 0.1 $\mathrm{M^{-1}}$ or less. If this were not the case, the steady-state approximation would not be appropriate and the reaction order in $\mathrm{ArCH_3}^{\bullet+}$ would be less than 2. Near the limit where rate law 18 is expected to hold it follows that $k_{16}[\mathrm{B}]$ must have a minimum value of about 10^8 $\mathrm{s^{-1}}$ (since $k_{16}K_{15}[\mathrm{B}] \sim 10^7$ $\mathrm{M^{-1}\ s^{-1}}$) to be consistent. If MeCN is B, this places a minimum value of about 5×10^6 $\mathrm{M^{-1}\ s^{-1}}$ on k_{16}. This would appear to be compatible with what might be expected for the deprotonation of the dication.[47] (Slow proton-transfer reactions from carbon have been observed, especially in aqueous solution. It has been argued that the complicating factor in these cases is associated with the protonation of an anion which is strongly hydrogen bonded.[47] In the reactions discussed here neither of the bases are anionic, and such effects are greatly diminished in aprotic solvents.)

(v) The near independence of k_{app} on the water concentration can also be explained by this mechanism. Since acetonitrile is present in concentrations greater than 125 times $[\mathrm{H_2O}]$, k_{16} would have to be about 125 times greater when B is water in order for water to compete as a base in this system. This would bring k_{16}

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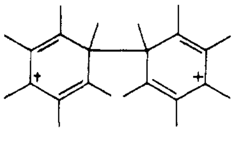
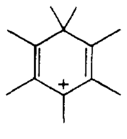
up close to the diffusion-controlled limit, which is not necessarily expected for the loss of a proton from carbon.[47] Since (16) is a very fast reaction, the dication would not be expected to show a very high degree of selectivity in reactions with bases. The fact that the addition of TFA up to about 1% has no observable effect on the rate supports the suggestion that water is not the active base.

Dimer Dication Structures. The substrate here is considered to be HMB, but similar intermediates are also possible for the reactions of PMB and DU. The first possibility that comes to mind is the symmetrical dimer **1** which has some of the features of the heptamethylbenzenium ion **2**, which is readily isolated as the $AlCl_4^-$ salt.[48] Structure **1** might well be expected to undergo the required chemistry, i.e., lose a proton (probably from a methyl group at a positively charged ring position), and the resulting cation could then undergo dissociation to the benzyl cation and substrate. The dimer dication is sterically crowded, and this should facilitate the decomposition reaction. This structure also is attractive from the nature of side products which have been observed from less highly substituted methylarene cation radicals. Dehydro dimers are frequently observed when there are unsubstituted ring positions.[49]



1



2

An important consideration in the likelihood of a particular intermediate is the kinetic requirements for its formation. In this case, a K_{15} of 10^{-1} or less under conditions where k_{app} is of the order of 10^7 M^{-1} s^{-1} requires that k_{15} be greater than 10^7 M^{-1} s^{-1}. Although rate constants greater than 10^8 M^{-1} s^{-1} have been observed for cation radical dimerization,[50] a K_{app} of 10^7 M^{-1} s^{-1} for the formation of **1** may appear somewhat larger than expected. However, the transition state to the formation of **1** could involve a parallel-plane arrangement which has not yet begun to feel the steric crowding of the methyl groups. This suggests a possible alternative structure for the dimer dication. The parallel-plane arrangement can be considered to be a π-complex which could undergo deprotonation without ever forming the fully bonded dimer **1**. There is ample precedent for the need to consider such complexes during cation radical reactions in order to explain kinetic results.[51] Even for the apparently simple anion radical dimerization (AN–X is a 9-substituted anthracene) in eq 21, the observation of negative activation energies requires an intermediate, which has been formulated as a π-complex.[43] Thus, it would appear that dimer dication **1** or a π-complex on the pathway to its formation are likely structures for the intermediate, the formation of which results in the negative activation energies.

$$2AN\text{–}X^{\bullet-} \underset{k_{-21}}{\overset{k_{21}}{\rightleftarrows}} (AN\text{–}X)_2^{2-} \qquad (21)$$

Comparison with Reactions of Cation Radicals Generated by Other Means. Direct deprotonations of methylarene cation radicals apparently do take place during metal-ion oxidation in nonaqueous media[1-5,17b] and during pulse radiolysis in aqueous solution.[6] During metal-ion oxidation, the cation radicals are generated in a thermodynamically unfavorable equilibrium (eq 22) with substrates present in rather low concentrations during kinetic studies This means that the cation radical concentrations are exceeding low so that dimerization cannot compete with the direct deprotonation. The pulse-radiolysis reactions also involve rather low concentrations of cation radicals and are carried out in a much more basic medium as well. Thus, there does not appear to be any inconsistency in the fact that two different mechanisms occur in the very different types of experimental situations.

$$ArCH_3 + M^{n+} \rightleftarrows ArCH_3^{\bullet+} + M^{m+} \qquad (22)$$

Comparison of the Observed Kinetics with Those from a Closely Related Rate Law. The kinetic results reported here are similar in many respects to some well-established results in proton-transfer reactions.[52] A particularly striking resemblance is found with the kinetics of the protonation of some benzylic anion intermediates by methanol (eq 23 and 24).[53] When Ar was *p*-nitrophenyl, k_H/k_D was observed to vary from 11.3 at –70 °C to 6.44 at +25 °C. This was attributed to the fact that neither K_{23} nor k_{24} in eq 25 is clearly rate limiting.[53] Equation 25 is nearly identical in form with rate law 17, which we propose for the deprotonation reactions of the cation radicals. Thus, our interpretation that the changes in k_H/k_D with temperature arise when neither reaction 15 nor reaction 16 is clearly rate determining is fully in accordance with the interpretations of Koch.[52,53]

$$\text{MeOH} + \text{Ar–C}^-\text{H–CF}_2\text{OMe} \underset{k_{-23}}{\overset{k_{23}}{\rightleftarrows}} \text{MeOH}\cdots\text{CH(Ar)–CF}_2\text{OMe} \qquad (23)$$

$$\text{MeOH}\cdots\text{CH(Ar)–CF}_2\text{OMe} \xrightarrow{k_{24}} \text{CH}_2\text{(Ar)–CF}_2\text{OMe} + \text{MeO}^- \qquad (24)$$

$$k = k_{23}k_{24}/(k_{-23} + k_{24}) \qquad (25)$$

Conclusions

The electrode kinetic studies show that the cation radicals of HMB, PMB, and DU clearly undergo second-order reactions in acetonitrile with rate constants of the order of 10^7 M^{-1} s^{-1}. The kinetic isotope effect data as well as the apparent negative activation energies can only be explained by a complex mechanism most likely involving a preequilibrium dimerization before proton loss. A symmetrical dimer dication (**1**) or a dimeric π-complex are possible structures for the intermediate. The fact that a first-order deprotonation takes place in other types of experiments, i.e., metal-ion oxidations or pulse radiolysis, is a consequence of the large differences in cation radical concentrations and in some cases the more basic medium that the reactions are carried out in.

Experimental Section

The substrates, HMB, PMB, and DU, were reagent grade and used without further purification. HMB-d_{18} was obtained from MSD Isotopes and contained 99.4 atom % D. Acetonitrile was refluxed for 12 h over P_2O_5 and then distilled. Me_4NBF_4 was reagent grade and dried at 120 °C before use.

The instrumentation and data-handling procedures as well as cells and electrodes were similar to those described in previous publications.[19,54]

Registry No. HMB, 34473-51-3; PMB, 79245-97-9; DU, 34473-49-9; D, 7782-39-0.

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