Acta Chemica Scandinavica B 34 (1980) 537–543

Short Communications

On the Mechanism of the Deprotonation of Alkylbenzene Cation Radicals in Acetonitrile

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The electrode mechanism for the formation of benzyl derivatives during oxidation of alkylbenzenes is complex and consists of the following steps (eqns. 1–4). The reactions are normally discussed in terms of the simple ECE(nuance) mechanism where the rate determining step is reaction (2) and reactions (3) and (4) are fast.[1] Work recently reported from this laboratory indicates that in the case of hexamethylbenzene (HMB) in dichloromethane-trifluoroacetic acid (TFA), reaction (3) contributes to the rate determining steps.[2] The latter was attributed to the effect of the strong acid, TFA, on the position of equilibrium (2).

$$\mathrm{Ar-CH_3} - e \rightarrow (\mathrm{Ar-CH_3})^{\cdot +} \qquad (1)$$

$$(\mathrm{Ar-CH_3})^{\cdot +} + \mathrm{B} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{Ar-CH_2^{\cdot}} + \mathrm{BH^+} \qquad (2)$$

$$\mathrm{Ar-CH_2^{\cdot}} + (\mathrm{Ar-CH_3})^{\cdot +} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \mathrm{Ar-CH_2^+} + \mathrm{Ar-CH_3} \qquad (3)$$

$$\mathrm{Ar-CH_2^+} + \mathrm{Nu} \xrightarrow{k_4} \text{products} \qquad (4)$$

We now report preliminary results of a kinetic study of the deprotonation of HMB and durene (DUR) cation radicals under acidic and neutral conditions in acetonitrile (AN) which force the unexpected conclusion that the reaction is second order in cation radical under both sets of conditions.

The results of a linear sweep voltammetry (LSV) study of the oxidation of HMB and DUR in AN containing TFA (5 %) and in AN over neutral alumina are summarized in Table 1. In all cases, d E^{p}/d log v which reflects the dependence of the peak potential on the voltage sweep rate (v), was near the theoretical value, 19.7 mV at 298 K, for a second order mechanism. On the other hand, d E^{p}/d log C° where C° is the substrate concentration, was observed to be small but not exactly zero. Rate determining deprotonation (eqn. 2) would require d E^{p}/d log v to be equal to 29.6 mV and likewise predicts independence of the substrate concentration.

Application of the steady state approximation on $\mathrm{Ar-CH_2^+}$ leads to rate law (5) which reduces to (6) when $k_4/k_{-3} \gg [\mathrm{Ar-CH_3}]$ and to (7) when $k_4/k_{-3} \ll [\mathrm{Ar-CH_3}]$. The simplified rate expressions

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Table 1. LSV mechanism analysis of the deprotonation of alkylbenzene cation radicals in acetonitrile.

Cation Radical	Conditions	$dE^{p}/d\log v^{a}$	$dE^{p}/d\log C^{\circ a}$
$\mathrm{HMB}^{\cdot +}$	AN–TFA[b]	21.0±0.9	5.7±0.9
$\mathrm{HMB}^{\cdot +}$	AN[c]	18.9±1.7	6.5±4.8
$\mathrm{DUR}^{\cdot +}$	AN–TFA[b]	20.7±1.1	1.3±0.6
$\mathrm{DUR}^{\cdot +}$	AN[c]	18.9±1.7	3.1±2.0

[a] Values in mV, measurements made by analog differentiation of the current-voltage response according to Ref. 7. [b] Solvent ratio (19/1) containing $\mathrm{Bu_4NBF_4}$ (0.1 M). [c] Solvent containing $\mathrm{Bu_4NBF_4}$ (0.1 M), experiments conducted over neutral alumina as described in Ref. 8.

0302-4369/80/070537-02$02.50

$$-\mathrm{d}[\mathrm{Ar-CH_3^{\cdot+}}]/\mathrm{d}t = \frac{2k_4K_2K_3[\mathrm{Ar-CH_3^{\cdot+}}]^2[\mathrm{Nu}][\mathrm{B}]/[\mathrm{BH^+}]}{k_4/k_{-3}[\mathrm{Nu}]+[\mathrm{Ar-CH_3}]} \quad (5)$$

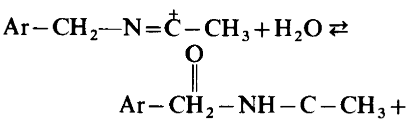
$$-\mathrm{d}[\mathrm{Ar-CH_3^{\cdot+}}]/\mathrm{d}t = 2k_3K_2[\mathrm{Ar-CH_3^{\cdot+}}]^2[\mathrm{B}]/[\mathrm{BH^+}] \quad (6)$$

$$-\mathrm{d}[\mathrm{Ar-CH_3^{\cdot+}}]/\mathrm{d}t = \frac{2k_4K_2K_3[\mathrm{Ar-CH_3^{\cdot+}}]^2[\mathrm{Nu}][\mathrm{B}]/[\mathrm{BH^+}]}{[\mathrm{Ar-CH_3}]} \quad (7)$$

(6) and (7) may be used to predict the values of dE^p/d log v and d E^p/d log $C°$ according to the rules recently formulated[3] based on earlier theoretical studies. The mechanisms corresponding to both (6) and (7) predict d E^p/d log v to be equal to 19.7 mV. However, the two mechanisms differ with regard to predictions of d E^p/d log $C°$.* Rate determining electron transfer [eqn. (3) and rate law (6)] predicts a slope of 19.7 mV while rate determining reaction of the benzylic cation [eqn. (4) and rate law (7)] leads to the predicition of zero slope.

The data appear to be inconsistent with rate determining electron transfer. Thus, we conclude that under the conditions of the measurements, reaction (4) contributes to determining the rate and rate law (7) best describes the kinetics of the reaction. The fact that d E^p/d log $C°$ was not zero could indicate that reaction (3) does influence the rate to some extent and eqn. (7) is an oversimplification of eqn. (5). The products of the oxidations are the corresponding benzyl acetamides.[4] In the reactions studied here, (4) corresponds to eqns. (8) and (9) and water is required to complete the reaction.

$$\mathrm{Ar-CH_2^+ + N{\equiv}C-CH_3 \rightleftarrows Ar-CH_2-N{=}C^+-CH_3} \quad (8)$$



$$\mathrm{Ar-CH_2-N{=}\overset{+}{C}-CH_3 + H_2O \rightleftarrows Ar-CH_2-NH-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 + H^+} \quad (9)$$

It seems most likely that under our conditions, the rate of (9) is severely decreased by the scavenging of water by TFA and alumina.

The results obtained in acetonitrile make it necessary to re-examine the conclusions made on the mechanism of the deprotonation of HMB cation radical in CH_2Cl_2-TFA.[2] In that case, the product forming reaction (4) involves TFA as the nucleophile.[5,6] It now seems most reasonable to consider the possibility that the latter is rate determining rather than the electron transfer step (3) as previously[2] suggested. Furthermore, the apparent discrepancy between our studies and those previously reported[1] can probably be accounted for by differing activities of nucleophiles present.

Acknowledgement. We thank the Swiss National Science Foundation for a post-doctoral fellowship for RSB.

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Received April 28, 1980.

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* The concentration dependence is especially well defined for the acid case where the buffer ratio, (B)/(BH$^+$) where B is AN in this case, is constant in the presence of excess TFA.