Relative Rate Constants for Anodic Oxidations of Potassium Alkanecarboxylates

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Abstract: Relative rate constants for electrolyses of potassium alkanecarboxylates were obtained by competitive electrolyses. In water large carboxylates electrolyzed faster than small ones, while in methanol no such difference was noted; this is considered in terms of solubility differences at the anode surface. For a given molecular weight group the nature of the alkyl radical generated (primary, secondary, or tertiary) exerted little influence on the rate of electrolysis; this is taken as evidence for carboxylate radical intermediacy.

Anodic discharge of carboxylates is generally believed to lead initially to carboxylate radicals.[1-9] However, Eberson[10] has suggested that free carboxylate radicals are not intermediates, but instead proposed a concerted electron transfer and loss of carbon dioxide.

$$RCO_2^- \longrightarrow [R\text{---}CO_2\text{---}e(\text{anode})]^{\ddagger} \longrightarrow R\cdot + CO_2 + e$$

Conway and Vijh[8] have criticized Eberson's proposal for not having considered the possibility of carboxylate radicals adsorbed on the anode surface.

To the extent that the transition state for electron transfer from anion to anode resembles RCO_2^- and/or $RCO_2\cdot$ the nature of R should have little effect on the electrolysis rate. The Eberson hypothesis would be consistent with easier discharge of RCO_2^- with more stable $R\cdot$. This possibility was examined by carrying out competitive electrolyses of mixtures of carboxylates.

Solutions of potassium carboxylates (1.0 *M*) and potassium hydroxide (0.2 *M*) were electrolyzed at bright Pt electrodes (Figure 1); the relative compositions of the starting and recovered acid mixtures were determined by vapor phase chromatography (28% diethylene glycol adipate and 3% H_3PO_4 on 60–80 mesh Firebrick; column temperature 105–200° at 0.9°/min). Control experiments demonstrated that little fractionation occurred during recovery of acids. Internal standards were used and corrections were applied for the thermal conductivity responses of the individual acids.

Results and Discussion

Large variations of current, voltage, anode potential, temperature, extent of electrolysis (7–77%), and concentrations of individual carboxylates (initial concentrations: 90–330 m*M*) yielded relative rates with poor reproducibility. However, under no circumstances, for a given molecular weight group and a given set of conditions, did the relative rates significantly increase as R on RCO_2^- was varied from primary to secondary to tertiary. Relative first-order rate constants are listed in Table I. Two points are evident: (1) within a given molecular weight group the nature of the alkanecarboxylate exerts little influence on the magnitude of the rate constant, and (2) in water solvent a carboxylate with a higher molecular weight has a larger rate constant than a lower molecular weight carboxylate; in methanol all carboxylates are discharged at the same rate.

Table I. Relative First-Order Rate Constants for Electrolyses of Potassium Carboxylates[a]

Potassium Carboxylate	Rel first-order rate constant[a] In water[b]	 In methanol[c]
Acetate[d]	<0.4[d]	. . .
Propanoate	0.4 ± 0.1	. . .
Butanoate	0.6 ± 0.1	1.3 ± 0.1
2-Methylpropanoate	0.7 ± 0.1	. . .
Pentanoate[e]	1.0[e]	1.0[e]
2-Methylbutanoate	1.1 ± 0.1	1.0 ± 0.2
2,2-Dimethylpropanoate	1.2 ± 0.1	1.0 ± 0.2
Hexanoate	1.8 ± 0.3	0.9 ± 0.01
2-Methylpentanoate	1.7 ± 0.1	. . .
2,2-Dimethylbutanoate	1.9 ± 0.2	. . .
Heptanoate	3.6 ± 1.1	1.0 ± 0.1
2,2-Dimethylpentanoate	3.1 ± 0.6	. . .
Octanoate	5.8 ± 2.5	1.0 ± 0.02

[a] $k/k' = (\log [RCO_2^-]_{\text{final}} - \log [RCO_2^-]_{\text{initial}})/(\log [R'CO_2^-]_{\text{final}} - \log [R'CO_2^-]_{\text{initial}})$. [b] Total initial $[RCO_2K]$ = 1.0 *M*; individual initial $[RCO_2K]$ = 0.09–0.3 *M*; [KOH] = 0.1–0.25 *M*; current = 0.1–3.8 amp; voltage = 4–20 V; anode potential = 1.3–3.9 V *vs.* sce; temperature = 25–75°; extent of reaction: 30–77% of total RCO_2K electrolyzed. [c] Total initial $[RCO_2K]$ = 0.7–1.0 *M*; individual initial $[RCO_2K]$ = 0.1–0.3 *M*; $[CH_3OK]$ = 0.6–0.7 *M*; current = 0.8–2.8 amp; voltage = 10–30 V; temperature = 25–65°; extent of reaction: 15–30% of total RCO_2K electrolyzed. [d] J. T. Keating, Department of Chemistry, The Pennsylvania State University, unpublished results. [e] The relative first-order rate constant for electrolysis of potassium pentanoate was arbitrarily chosen to be 1.0.

The first point suggests that the stability of the alkyl radical formed in anodic oxidations of alkanecarboxylates plays no part in determining the rate of oxidation. If there had been bond breaking during the electron transfer those carboxylates producing tertiary alkyl radicals would have been preferentially discharged. This was not observed. Therefore, electron

$$RCO_2^- \longrightarrow (R\text{--}CO_2)\cdot + e^-$$

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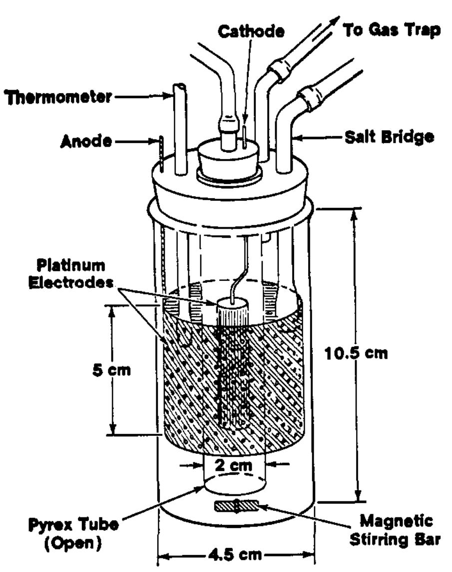

Figure 1. Electrolysis cell.

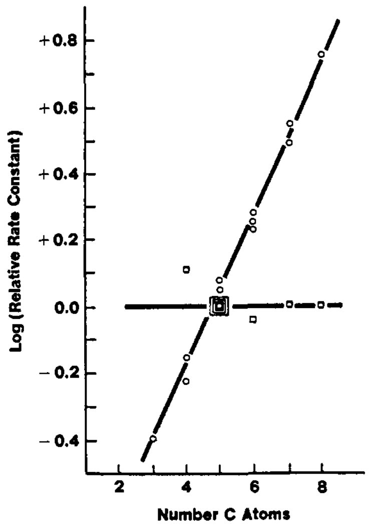

Figure 2. First-order anodic oxidation rate constant *vs.* molecular weight of carboxylate; solvent: water, ○; methanol, □.

transfer from RCO_2^- does not lead directly to $R\cdot$, rather to $RCO_2\cdot$, free or adsorbed.[5]

The second point was not anticipated. Indeed, if any relationship between rate of electrolysis and molecular weight had been expected, a trend opposite to that shown in Figure 2 would have been predicted, since diffusion coefficients of carboxylates decrease with increasing molecular weight (strictly speaking, with increasing molecular volume).[11] A correlation between the rates of discharge in water solution and the solubilities of tetraalkylammonium perchlorates[12] (Figure 3) is apparent. The results suggest the possibility that the rates of discharge in water solutions are related to carboxylate solubilities in nonaqueous solvents. Hydrophopic organic materials (hydrocarbons, alcohols, esters) are produced at the anode during electrolyses. This layer would fractionate the carboxylates, dissolving more of the higher molecular weight ions and thus making them more available for oxidation. Alternatively, there may be specific adsorption effects which favor adsorption on the anode surface; little is known about this possibility.

Anodic oxidations of alkyl carboxylates in methanol exhibit simple behavior; all oxidize at the same relative rate. A mechanism for anodic oxidations of carboxylates is detailed elsewhere.[9]

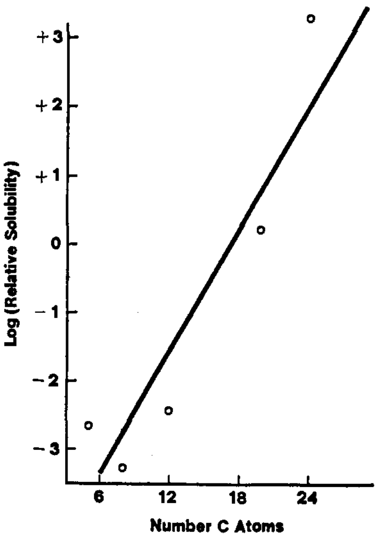

Figure 3. Relative solubility (benzene–water) of tetraalkylammonium perchlorates *vs.* molecular weight.[12]

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