Studies on the Kolbe Electrolytic Synthesis

IV *. A Theoretical Investigation of the Mechanism by Standard Potential Calculations

LENNART EBERSON

Department of Organic Chemistry, University of Lund, Sweden

Standard potentials have been calculated for a number of electrode processes possibly involved in the anodic oxidation of salts of carboxylic acids. By comparison with available experimental data it is concluded that the primary electrode reaction is

$$RCOO^- \rightarrow R\cdot + CO_2 + e$$

followed by a further oxidation of the radical to a carbonium ion

$$R\cdot \rightarrow R^+ + e$$

in those cases where the ionization potential of the radical (as determined by the electron impact method) is lower than about 8 eV.

The Kolbe electrosynthesis is a convenient tool for the preparation of many otherwise difficultly accessible compounds.[1-3] Much interest has been devoted to the elucidation of its mechanism and it is now generally believed that the primary step consists of discharge of the carboxylate ion at the anode

$$RCOO^- \rightarrow RCOO\cdot + e \qquad (1)$$

with subsequent decarboxylation of the acyloxy radical (2).

$$RCOO\cdot \rightarrow R\cdot + CO_2 \qquad (2)$$

The Kolbe product R—R is formed by combination of two radicals R·, and the by-products in many cases are easily accounted for by other radical reactions, *i.e.* disproportionation of R· or attack of R· on C—H bonds in solvent or solute molecules.

Electrolyses carried out under controlled anode potential conditions indicate that the reaction occurs significantly only above a certain limiting value of the electrode potential.[1-44] It has been suggested that the critical potential

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* Part III. *Acta Chem. Scand.* **17** (1963) 1196.

originates from the formation of a surface film of intermediates at the anode rather than the requirement of a critical discharge potential for the carboxylate ion.

During the last five years much evidence has accumulated that a second one-electron transfer to the anode is possible in a number of cases,[15-20] involving oxidation of the intermediate radical R· to a carbonium ion.

$$R\cdot \rightarrow R^+ + e \qquad (3)$$

By choice of suitably substituted carboxylic acids many of the typical carbonium ion rearrangements have been demonstrated during conditions of Kolbe electrolysis.[16-19] Also, many of the earlier experimental findings which do not fit into the pattern of the radical theory can be unambiguously interpreted by assuming the intervention of carbonium ions.[18]

With at least two possible electrode processes it is of immediate interest to know which experimental and structural factors are relevant for the successful application of the Kolbe synthesis, here defined as the preparation of the coupled product R—R by the radical reaction:

$$2 R\cdot \rightarrow R—R \qquad (4)$$

Conversely, it would be of interest to utilize reaction (3) for the study of carbonium ion reactions and, if possible, to find some preparative use for this reaction path.

This paper deals with the calculation of standard potentials for the electrode processes (1), (3), (5), (6), and (7) in those cases where reasonably reliable thermodynamic data are accessible or can be estimated.

$$R—COO^- \rightarrow R\cdot + CO_2 + e \qquad (5)$$
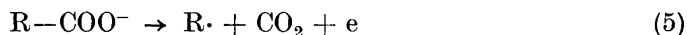
In reaction (5) the electron transfer to the anode and the decarboxylation are assumed to take place simultaneously. Process (6) is a two-electron transfer with simultaneous bond breaking to form a carbonium ion directly
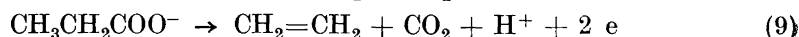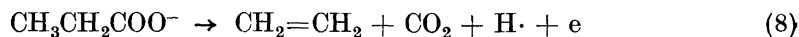
$$RCOO^+ \rightarrow R^+ + CO_2 + 2 e \qquad (6)$$
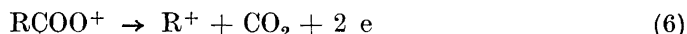
and (7) is a further oxidation of the acyloxy radical RCOO· with simultaneous bond breaking.

$$RCOO\cdot \rightarrow R^+ + CO_2 + e \qquad (7)$$
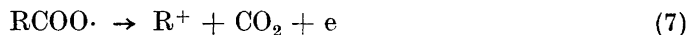
Unfortunately thermodynamic data for the species $RCOO^+$ are not available so that calculations for processes involving this ion could not be performed. It is probable that $RCOO^+$ is not capable of existing even for very short periods of time; at least it has never been observed in mass spectra of carboxylic acids or esters. For comparison, it may be mentioned that the half life-time of the acetoxy radical has been estimated as $10^{-9}-10^{-10}$ sec at $65°$.[21]

Furthermore, the standard potentials of two other electrode processes, (8) and (9), were calculated for propionate ion which has β-hydrogen atoms and may react according to mechanisms involving the simultaneous breaking of two bonds, formation of ethylene, and transfer of one or two electrons.

$$CH_3CH_2COO^- \rightarrow CH_2=CH_2 + CO_2 + H\cdot + e \qquad (8)$$

$$CH_3CH_2COO^- \rightarrow CH_2=CH_2 + CO_2 + H^+ + 2 e \qquad (9)$$

THERMOCHEMICAL CALCULATIONS

1. Electrode process $RCOO^-/RCOO\cdot$. In order to obtain the standard potential of the electrode process $RCOO^-/RCOO\cdot$ referred to the hydrogen electrode we must calculate the standard free energy change at 25° of the reaction (10):

$$RCOO^-(aq) + H^+(aq) \rightarrow RCOO\cdot(aq) + \tfrac{1}{2}H_2(g) \tag{10}$$
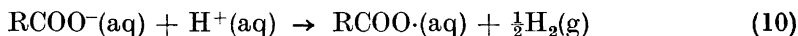
which requires the knowledge of standard enthalpies of formation and standard entropies of the species involved.[22] The data used are given in Table 1 together with the values of ΔH°, ΔS° and ΔG° for reaction (10) calculated by the set of equations (11)−(13).

$$\Delta H^\circ = \Delta H_f^\circ[RCOO\cdot](aq) + \tfrac{1}{2}\,\Delta H_f^\circ[H_2](g) - \Delta H_f^\circ[RCOO^-](aq) - \Delta H_f^\circ[H^+]\,(aq) \tag{11}$$

$$\Delta S^\circ = S^\circ[RCOO\cdot](aq) + \tfrac{1}{2}\,S^\circ[H_2](g) - S^\circ[H^+](aq) - S^\circ[RCOO^-](aq) \tag{12}$$

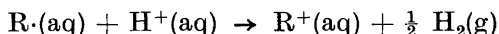$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{13}$$

The standard potential E° is finally obtained from the relationship $E^\circ = \Delta G^\circ/23.06$ and is given in the last column of Table 1. Calculations were made for $R = CH_3$, C_2H_5, n-C_3H_7 and C_6H_5, which are the only cases where data are available for the calculation of $\Delta H_f^\circ[RCOO\cdot](aq)$.[23]

2. Electrode process $RCOO^-/R\cdot + CO_2$. With relevant data from Table 1 and the values of $\Delta H_f^\circ[R\cdot](aq)$ and $S^\circ[R\cdot](aq)$ given in Table 2, the standard potentials for this electrode process were calculated for $R = CH_3$, C_2H_5, n-C_3H_7 and C_6H_5 in the same way as described above.

3. Electrode process $R\cdot(aq)/R^+(aq)$. ΔH° for this electrode process was calculated from the following set of equations:

$$R\cdot(g) \rightarrow R^+(g) + e(g) \qquad \Delta H_1 \tag{14}$$

$$R^+(g) \rightarrow R^+(aq) \qquad \Delta H_2 \tag{15}$$

$$R\cdot(g) \rightarrow R\cdot(aq) \qquad \Delta H_3 \tag{16}$$

$$\tfrac{1}{2}\,H_2(g) \rightarrow H^+(g) + e(g) \qquad \Delta H_4 \tag{17}$$

$$H^+(g) \rightarrow H^+(aq) \qquad \Delta H_5 \tag{18}$$
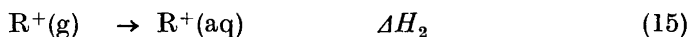
According to Hess' law, ΔH° for the reaction

$$R\cdot(aq) + H^+(aq) \rightarrow R^+(aq) + \tfrac{1}{2}\,H_2(g)$$

then is $\Delta H_1 + \Delta H_2 - \Delta H_3 - \Delta H_4 - \Delta H_5$.

The data used are given in Table 3 together with the calculated values of ΔH°, ΔS°, ΔG° and E° for reaction (3) in the case of $R = CH_3$, C_2H_5, n-C_3H_7, i-C_3H_7 and t-C_4H_9.

4. Other electrode processes. The standard potentials for (6) and (7) are obtained by appropriate combinations of the standard potentials of (1), (3) and (5). For the computation of E° of (8) and (9) the following values were used: $\Delta H_f^\circ[CH_2=CH_2](g) = 12.5$ kcal/mole,[38] $S^\circ[CH_2=CH_2](g) = 52.5$ e.u., heat of solution of ethylene in water approximated as that of ethane $= -4.0$ kcal/mole,[32] entropy of solution in water approximated as that of ethane =

Table 1. Data for the calculation of $\Delta H°$, $\Delta S°$, $\Delta G°$, and $E°$ for the electrode process RCOO$^-$/RCOO.

R	$\Delta H_f°$[RCOO$^-$] (aq) kcal/mole	$\Delta H_f°$[RCOO·] (aq) kcal/mole	$S°$[RCOO$^-$] (aq) e.u.	$S°$[RCOO·] (aq) e.u.	$\Delta H°$ kcal/ mole	$\Delta S°$ e.u.	$\Delta G°$ kcal/ mole	$E°$ V
CH$_3$	-116.1^a	-49.2^b	21.1^c	43.3^d	66.9	37.8	55.6	2.41
C$_2$H$_5$	-121.7^e	-59.1^f	21.1^g	43.3^h	62.6	37.8	51.3	2.23
n-C$_3$H$_7$	-128.2^i	-65.5^j	21.1^g	43.3^h	62.7	37.8	51.4	2.23
C$_6$H$_5$	-85.6^k	-37.0^l	35^k	54^m	48.6	34.6	38.3	1.66

^{a} From $\Delta H_f°$[CH$_3$COOH](liq) $= -115.7$ kcal/mole,[24] the heat of solution of liquid acetic acid in water $= -0.33$ kcal/mole,[25] and the heat of neutralization of acetic acid $= -0.07$ kcal/mole[26].

^{b} From $\Delta H_f°$[CH$_3$CO$-$O$-$O$-$COCH$_3$](liq) $= -127.9$ kcal/mole and D(O$-$O) $= 29.5$ kcal/mole,[23] assuming that the heat of solution of liquid acetyl peroxide in water is negligible.

^{c} Ref.[27]

^{d} Assumed to be equal to $S°$[CH$_3$COOH](aq).[20]

^{e} From $\Delta H_f°$[C$_2$H$_5$COOH](liq) $= -121.3$ kcal/mole,[28] the heat of solution of liquid propionic acid in water assumed to be equal to that of acetic acid $= -0.33$ kcal/mole, and the heat of neutralization of propionic acid $= -0.08$ kcal/mole.[26]

^{f} From $\Delta H_f°$[C$_2$H$_5$CO$-$O$-$O$-$COC$_2$H$_5$](liq) $= -148.2$ kcal/mole and D(O$-$O) $= 30.0$ kcal/mole,[23] assuming that the heat of solution of liquid propionyl peroxide in water is negligible.

^{g} In the absence of any data, the value for the acetate ion was used.

^{h} In the absence of any data, the value for the acetoxy radical was used.

^{i} From $\Delta H_f°$[n-C$_3$H$_7$COOH](liq) $= -127.2$ kcal/mole,[28] the heat of solution of liquid butyric acid in water assumed to be equal to that of acetic acid $= -0.33$ kcal/mole, and the heat of ionization of butyric acid $= -0.7$ kcal/mole.

^{j} From $\Delta H_f°$[n-C$_3$H$_7$CO$-$O$-$O$-$COC$_3$H$_7$-n](liq) $= -161.0$ kcal/mole and D(O$-$O) $= 30.0$ kcal/mole,[23] assuming that the heat of solution of liquid butyryl peroxide in water is negligible.

^{k} Ref.[29]

^{l} From the value of $\Delta H_f°$[C$_6$H$_5$COO·](g) calculated by Jaffe et al.,[23] assuming that the solvation enthalpy of gaseous benzoyloxy radical is the same as that of gaseous benzoic acid, -15.6 kcal/mole.[29,30]

^{m} Ref.[29]; assumed to be equal to $S°$[C$_6$H$_5$COOH](aq).

Table 2. Data for the calculation of $\Delta H°$, $\Delta S°$, $\Delta G°$, and $E°$ for the electrode process RCOO$^-$/R· $+$ CO$_2$.

	$\Delta H_f°$[R·](aq) kcal/mole	$S°$[R·](aq) e.u.	$\Delta H°$ kcal/mole	$\Delta S°$ e.u.	$\Delta G°$ kcal/mole	$E°$ V
CH$_3$	28.9^a	14.9^b	46.3	38.4	34.8	1.55
C$_2$H$_5$	21.0^a	25.5^b	44.0	49.0	29.4	1.28
n-C$_3$H$_7$	16.3^a	26.3^b	45.8	48.8	31.3	1.36
C$_6$H$_5$	63.2^c	31.8^d	50.1	59.7	32.3	1.40

^{a} From $\Delta H_f°$[R·](g)[31] and the heat of hydration of the gaseous radical, assumed to be equal to the heat of hydration of the parent gaseous hydrocarbon.[32]

^{b} From $S°$[R·](g)[33] and the entropy of hydration of the gaseous radical, assumed to be equal to the entropy of hydration of the parent gaseous hydrocarbon.[32]

^{c} From $\Delta H_f°$[C$_6$H$_5$·](g)[34] and the heat of hydration of the gaseous phenyl radical, assumed to be equal to the heat of hydration of gaseous benzene.[35]

^{d} From $S°$[C$_6$H$_5$·](g)[33] and the entropy of hydration of the gaseous phenyl radical, assumed to be equal to the entropy of hydration of gaseous benzene.[35]

Table 3. Data for the calculation of $\Delta H°$, $\Delta S°$, $\Delta G°$, and $E°$ for the electrode process $R\cdot/R^+$.

R	ΔH_1 kcal/ mole[a]	ΔH_2 kcal/ mole[b]	ΔH_3 kcal/ mole[c]	$S°[R^+](aq)$ e.u.[d]	$\Delta H°$ kcal/ mole[e]	$\Delta S°$ e.u.	$\Delta G°$ kcal/ mole	$E°$ V[f]
CH_3	229.4	−61	−3.1	42.7	80.4	43.4	67.5	2.92
C_2H_5	202.5	−54	−4.0	57.7	61.4	47.8	47.2	2.05
$n\text{-}C_3H_7$	200.4	−50	−5.7	65.0	65.0	54.3	48.8	2.11
$i\text{-}C_3H_7$	182.2	−46	−5.7	64.5	52.8	53.8	36.8	1.59
$t\text{-}C_4H_9$	171.1	−40	−6.0	69.4	46.0	55.6	29.4	1.27

[a] Ref.[36]
[b] Ref.[37]
[c] Ref.[32]
[d] From $S°[R\cdot](g)$ −1.4 e.u.[33] (due to the contribution from an assumed doublet ground state state in monoradicals) and the entropies of solvation of carbonium ions given in Ref.[37]
[e] $\Delta H_4 = 367.1$ kcal/mole,[38] $\Delta H_5 = -276$ kcal/mole.[39]
[f] Values calculated for the solvent methanol differ very little (data taken from Ref.[37]).

−33.6 e.u.,[32] $\Delta H_f°[H\cdot](aq) = 51.1$ kcal/mole,[40] $S°[H\cdot](g) = 27.4$ e.u. and the entropy of solution of the hydrogen atom in water approximated as that of helium $= -19$ e.u.[38,41]

All calculated standard potentials have been collected in Table 4.

Owing to the multiplicity and inhomogeneity of the thermodynamic data used in the calculation of standard potentials, the relative and absolute accuracy is difficult to estimate. Only for the key processes (1) and (3), R = CH_3, are thermodynamic data known with good accuracy and in these cases the absolute accuracy is estimated at ± 0.15 V. For the other reactions some data are either approximations from other molecules or based on theoretical computations. The use of such data is, however, well justified by the successful applications described in the literature,[33,37,40] which indicate that no serious errors are introduced in this way.

The use of ionization potentials determined by mass spectrometry (14) is likely to give too high values for processes (3), (6) and (7), since these ioniza-

Table 4. Standard potentials of processes possibly involved in the Kolbe electrolysis.

Electrode process

R	$RCOO^-/RCOO\cdot$ (1)	$R\cdot/R^+$ (3)	$RCOO^-/R\cdot$ $+ CO_2$ (5)	$RCOO^-/R^+$ $+ CO_2$ (6)	$RCOO\cdot/R^+$ $+ CO_2$ (7)	$C_2H_5COO^-/C_2H_4$ $+ CO_2 + H\cdot$ (8)	$C_2H_5COO^-/C_2H_4$ $+ CO_2 + H^+$ (9)
CH_3	2.41	2.92	1.55	2.24	2.06		
C_2H_5	2.23	2.07	1.28	1.68	1.11	1.92	0.31
$n\text{-}C_3H_7$	2.23	2.11	1.36	1.73	1.24		
$i\text{-}C_3H_7$		1.59					
$t\text{-}C_4H_9$		1.27					
C_6H_5	1.66		1.40				

tion potentials generally are higher by some 0.4 eV than those obtained by the photoionization method in the few cases these are known.[36]

These standard potentials also depend heavily on the value of the absolute enthalpy of hydration for the gaseous proton (18), which was taken as -276 kcal/mole from the work by Eigen and DeMayer.[39] If we instead use the value of -261 kcal/mole given by Halliwell and Nyburg [42] we arrive at standard potentials lower by some 0.6 V.

However, these sources of error work in the same direction and should only give the result that processes involving the formation of carbonium ions would be more favoured energetically.

DISCUSSION

The nature of the primary electrode process
A. The critical potential

The existence of a critical potential in the region 2.1—2.8 V for the formation of the Kolbe product R_2 has been established for a number of aliphatic acids in aqueous as well as non-aqueous solvents.[4-14] The current density-potential curve has the general appearance shown in Fig. 1 although in practice the inflection may be less marked. In aqueous solution, the part of the curve below the inflection corresponds to the oxygen evolution process and the part above the inflection to the Kolbe reaction.[10,11] In non-aqueous solvents data are very scarce but Conway and Dzieciuch [12] obtained a similar curve for 1 M CF_3COOK in anhydrous trifluoroacetic acid. In this case, contrary to electrolyses carried out in aqueous solution, the Kolbe product C_2F_6 was formed also *below* the inflection and no detectable oxygen evolution occurred.

In the electrolysis of propionate ion no break in the curve was observed except at a very high propionate concentration (5 M).[10] Again the Kolbe product, C_4H_{10} (together with ethane and ethylene), was formed only above the critical potential whereas ethylene was formed with high current efficiency below this potential. In those cases where reliable quantitative measurements have been made the log [current density]-potential plot in the region of Kolbe electrolysis obeys a Tafel equation with the Tafel constant reported to be 0.12 [14] or 0.13 V [11] for acetate ion.

From a study of current density-potential relationships in the electrolysis of acetate in aqueous solution and charging curve phenomena for platinum and iridium anodes in aqueous acetate solution, Dickinson and Wynne-Jones [11] suggested the following interpretation of the critical potential. At anode potentials below the critical potential oxygen evolution occurs as the sole electrode process, but as the anode potential is increased the electrode surface is covered by adsorbed acetoxy radicals produced by the discharge of acetate ions. When all "discharge sites" are occupied in this way the oxygen evolution is severely hindered and at a certain potential acetate ions begin to discharge on to already occupied discharge sites. This point is identified with the critical potential. The theory implies that an adsorbed acetoxy radical is a rather stable species and that the Kolbe reaction occurs only when an acetate ion is discharged upon an adsorbed acetoxy radical.

However, it seems highly improbable that an acetoxy radical would be stable under the conditions prevailing at the anode surface. The molecular orbital theory locates two π-electrons in the highest occupied molecular orbital (h.o.m.o.) of the carboxylate group and one electron in the h.o.m.o. of the carboxylate radical. In the simple Hückel treatment, these molecular orbitals have the same energy and consequently we would expect further oxidation of an adsorbed acetoxy radical under conditions which allow the discharge of the acetate ion. Thermodynamically this does not seem unreasonable, as is seen by comparison of the standard potentials for the RCOO⁻/RCOO· and RCOO·/R⁺ + CO_2 processes (Table 4).

The explanation of the critical potential given by Conway and Dzieciuch [12] involved the formation of a passive film of intermediates at the anode surface. This surface film is considered to be necessary for the steady state occurrence of the Kolbe reaction (although they somewhat contradictorily state that the Kolbe product is formed also below the region for the formation of the film). The break in the current-potential curve would correspond to the building up of the surface film.

In this paper we shall treat the critical potential in the following way. In aqueous solution anions are known to be involved in the oxygen evolution process at high anode potentials.[43] The factors which determine the extent of this effect are the potential, the nature and concentration of the anion and probably the anode material (only Pt has so far been investigated). The effect manifests itself in the form of breaks in Tafel plots (log[current density]-*versus* potential plots) and this indicates that a change in the oxygen evolution mechanism occurs in the transition region, above which isotope exchange experiments show that anions take part in the oxygen evolution process. This does not occur below the transition region. The exchange of ^{18}O was thought to occur under the influence of the surface film which forms at high overpotentials.

We shall assume an analogous interpretation of the critical potential for the Kolbe reaction in aqueous solution. In the transition region there occurs a change in the mechanism of oxygen evolution (oxygen is evolved over the whole potential region studied, irrespective of the Kolbe process [10,11]) due to the formation of a chemisorbed layer which in its turn is connected with the fact that carboxylate ions begin to discharge in the transition region. The adsorbed layer probably consists of adsorbed radicals R· which, dependent on the standard potential of the couple R·/R⁺ (3), may be oxidized further to carbonium ions or remain relatively stable on the electrode surface (see Table 4, and the discussion below).

This explains why only platinum and iridium anodes support the Kolbe process in aqueous solution.[11] On these metals chemisorbed layers form above a certain anode potential with a resultant large oxygen overpotential. On a less noble metal an oxide film is formed in the early stages of the log-E curve. The oxygen overpotential is relatively smaller on oxide films than chemisorbed layers [43] and the anode potential cannot be increased to such high values that carboxylate ions begin to discharge.

In non-aqueous solvents the oxygen evolution process is excluded which means that the choice of anode material becomes less critical. The explanation

of the critical potential given by Conway and Dzieciuch [12] here appears to be satisfactory.

Whether the critical potential observed in the Kolbe reaction represents a critical potential for the discharge of the anion, as is upheld by many investigators,[5-10] is difficult to decide on the basis of existing data. From the quantum chemical point of view it appears reasonable that a critical potential would exist. For the process

$$ArO^- \rightarrow ArO\cdot + e \qquad (19)$$

Fieser [44] has determined a reproducible anodic potential which is thought to represent the point where the aryloxy ion commences to be discharged. A plot of Fieser's critical potentials for phenols *versus* the charge density of the exocyclic carbon of the isoconjugate carbanions ($ArCH_2^-$) gives a good linear relationship from which the value of $1.2-1.5$ was deduced for the h-parameter of a charged oxygen atom donating two electrons ($h_{\ddot{o}^-}$).[45,46] We also know that for many polarographic oxidation and reduction processes the half-wave potential is linearly correlated with the energy coefficient of the highest occupied and lowest empty molecular orbital, respectively.[47] Such linear relationships are similarly obtained between ionization potentials as determined by the electron impact method and the energy coefficient of the h.o.m.o. of various hydrocarbons and radicals.[47] Especially the analogy between the ionization of a radical in the mass spectrometer and the irreversible anodic electron capture from an anion is an indication that there exists a critical discharge potential for an anion just as well as the production of R^+ from $R\cdot$ under electron bombardment occurs significantly only above the ionization potential.

In order to get an idea of the variation in energy of the h.o.m.o. of a carboxylate ion with the structure of the rest of the molecule the energy coefficient for the h.o.m.o. was calculated by the LCAO—MO method (Table 5). Two parameter sets were used: (I) $\alpha_O = \alpha + 2\beta$,[48] $\beta_{C\text{-}O} = \sqrt{2}\,\beta$ [48] and $\alpha_C = \alpha + h_i\beta$, where h_i is -0.5, -0.4, $\ldots 0 \ldots + 0.4$, $+0.5$, and (II) $\alpha_O = \alpha + 1.2\,\beta$ [45,46] $\beta_{CO} = \beta$ and α_C as in (I). The benzoate ion was also included using (I) and (II) with $h_i = 0$. By the variation in h_i over the interval $-0.5-+0.5$ we cover all possible cases of variations in the carboxylate ion energy levels due to variation in inductive effects from the rest of the molecule. As an example, $h_i = -0.5$ represents the inductive model of hyperconjugation in acetate ion, and $h_i = 0.3$ accounts for the inductive effect from the fluorine atoms in trifluoroacetate ion (with $h_F = 3$).

Table 5 shows the energy coefficients, m_2, of the h.o.m.o. of carboxylate ions using the parameter sets defined above. If the potential-determining step simply consists of the removal of one π-electron from the h.o.m.o. of the carboxylate group without simultaneous bond breaking (1), we would predict a linear correlation between m_2 and the critical potential. At least in principle it should be possible to test this theory by measuring the critical potentials of some properly substituted acids, but a closer examination of Table 5 reveals that both experimental and theoretical difficulties are encountered in such an investigation. Firstly, for all ions except the benzoate ion the total variation in m_2 is rather small with both parameter sets (0.067 and 0.090). By comparison with LCAO—MO calculations for other electrolytic oxidation and reduction

Table 5. Energy coefficients of the highest occupied molecular orbital of $R-COO^-$ (m_2 in $\varepsilon_2 = a + m_2\beta$).

h_i	Parameter set	
	I	II
0.5	1.893	1.135
0.4	1.886	1.125
0.3	1.879	1.116
0.2	1.872	1.107
0.1	1.866	1.098
0	1.859	1.089
−0.1	1.851	1.080
−0.2	1.845	1.071
−0.3	1.839	1.062
−0.4	1.832	1.053
−0.5	1.826	1.045
benzoate ion	1.349	1.069

processes we may conclude that this small variation is likely to reflect itself in rather small differences in the critical potentials (within a range of about 0.2 V). With the inherent experimental difficulties of determining critical potentials accurately such an investigation will probably not give any conclusive results. Secondly, for the benzoate ion the theory predicts quite different results dependent on the choice of parameters, which also would make any interpretation of measurements of critical potentials ambiguous.

B. T h e r m o d y n a m i c - k i n e t i c   a p p r o a c h   t o   t h e   n a t u r e   o f   t h e   e l e c t r o d e   p r o c e s s

As mentioned in the introduction both radical and carbonium ion intermediates have been shown to participate in the chemical reactions accompanying the anodic oxidation of a carboxylate ion $RCOO^-$. Dependent on the structure of the acid we may obtain products resulting from (a) pure radical processes (b) pure carbonium ion processes and (c) a combination of both types. The electrolysis of acetate ion in aqueous solution at slightly acid pH appears to belong to the first type of reaction. We are now in the position to discuss the nature of the potential-determing electrode process. Two possibilities exist, namely discharge of the acetate ion with formation of the acetoxy radical (1) which then decarboxylates in a second chemical step (2), or a process involving electron transfer and simultaneous breaking of the C—C bond between the methyl and carboxylate group (5). For these processes the calculated standard potentials are 2.41 and 1.55 V, respectively (Table 4).

Vasilev and Fiochin [14] empirically found the following relationship between applied potential E, current density I (amp/cm^2) and acetate ion activity a_{AcO^-} (here expressed in mole/cm^3) under conditions of Kolbe electrolysis (*i.e.* on the upper part of the curve in Fig. 1).

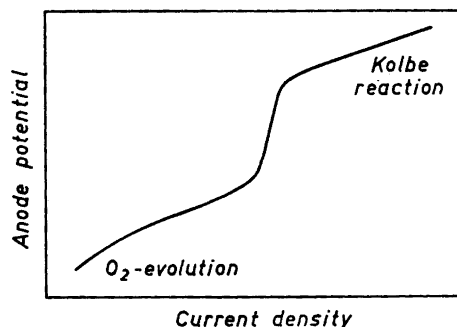$$E = 2.07 + 0.12 \log I - 0.12 \log a_{AcO^-} \tag{20}$$

Fig. 1. Showing the general appearance of the current density *versus* anode potential curve for the Kolbe reaction.

This is a Tafel equation and the fact that the process obeys such a relationship is a proof of the irreversible nature of the electrode reaction.

Theoretically, an irreversible anode reaction is approximately described by eqn. (21) provided the current resulting from the reverse process can be neglected.[49],[50] This is certainly the fact in the Kolbe electrolysis of acetate where the concentration of the oxidized form ($RCOO\cdot$ or $R\cdot$) is negligible.

$$i = n \, F \, A \, C_R k_{s,h} \, \exp \, \frac{(1-\alpha) \, n_a F \, (E-E^\circ)}{RT} \tag{21}$$

In eqn. (21) i is the current in amperes, n is the number of Faradays consumed in the oxidation of one mole of the reduced form, A the area of the anode (cm²), C_R is the concentration of the reduced from at the anode surface (mole/cm³), $k_{s,h}$ the common rate constant of the forward and reverse processes at the standard potential of the process, R the gas constant, T the absolute temperature, α the transfer coefficient, n_a the number of electrons involved in the rate-controlling step, E the applied potential and E° the standard potential of the couple. Upon rearrangement of (21) we obtain

$$E = E^\circ - \frac{RT}{(1-\alpha) \, n_a F} \ln nF k_{s,h} + \frac{RT}{(1-\alpha) \, n_a F} \ln I - \frac{RT}{(1-\alpha) \, n_a F} \ln C_R \tag{22}$$

For the processes discussed here $n = n_a = 1$ and we then must put $\alpha = 0.5$ and $E^\circ - \dfrac{RT}{(1-\alpha) \, n_a F} \ln Fk_{s,h} = 2.07$ in order to equate (22) term for term with the empirical relationship (20). We also must assume that C_R is equal to the activity of acetate ion in the bulk of the solution, which is permissible in this approximate treatment. This gives us

$$E^\circ - 2.07 = 0.12 \log Fk_{s,h} \tag{23}$$

For $E^\circ = 2.41$ V (1), $k_{s,h}$ is of the order 10^{-2} cm/sec and for $E^\circ = 1.55$ V (5) of the order 10^{-9} cm/sec. Clearly the process (5) has all the characteristics of an irreversible electrode reaction requiring a considerable overpotential to occur with a measurable rate. On the other hand, process (1) would be almost reversible, as judged from the value of $k_{s,h}$[50] and this contradicts all experimental experience.

Thus, the empirical equation (20) fits best with the assumption that the potential-determing step in the Kolbe reaction for acetate ion in aqueous solution is an irreversible one-electron transfer with simultaneous bond-breaking (5).

We shall not attempt to discuss the behavior of aqueous propionate and butyrate upon electrolysis in detail as available current density-protential data are not sufficient for such a discussion. However, it is quite evident that at least two electrode processes are involved in the propionate electrolysis, one occurring at lower anode potentials giving only ethylene [via (9)?] and one at higher potentials giving the Kolbe product butane in low yield [via (5)].[10] The same is probably true for butyrate.[10]

For an aromatic acid, in this investigation exemplified by benzoic acid, the situation is quite a different one. The benzoyloxy radical is a fairly stable species with a rate constant for decarboxylation of the order of 1 sec^{-1} (calculated from the rather approximate value of the activation energy given by Cook and Depatie [51]). Accordingly it is probable that the primary electrode reaction in the electrolysis of benzoate ion is (1), R = phenyl ($E° = 1.40$ V) and that the benzoyloxy radical then diffuses out into the bulk of the solution with subsequent decarboxylation or attack on solvent or solutes present. The very low or zero yield of the Kolbe product and the preference for formation of homolytically arylated products [52] is consistent with this mechanism.

In conclusion: several anode processes are thermodynamically feasible in the electrolysis of a carboxylate $RCOO^-$, dependent on the nature of R, the anode potential, the solvent, and the anode material. Each acid will probably require a separate study for a detailed mechanistic interpretation but some predictions from standard potential data may serve as useful guides in the preparative utilization of the Kolbe synthesis. These will be considered in the next section.

Implications for the preparative use of the Kolbe reaction

The preparative Kolbe reaction is usually carried out in a non-aqueous solvent, e.g. methanol, where experimental factors are less critical than in water. In a non-aqueous solvent we shall assume that the primary electrode process is (5) followed by (3) if this is thermodynamically favored. Thus, the reaction scheme is entirely analogous to that of the cathodic reduction of alkyl halides [(24) and (25)] and conforms to the general mechanism for organic electrode processes given by Elving and Pullman.[53]

$$R - X + e \rightarrow R\cdot + X^- \tag{24}$$

$$R\cdot + e \rightarrow R^- \tag{25}$$

Furthermore, we shall assume that (5) requires a high anode potential to go with measurable rate and that this potential is relatively independent of the nature of R, except when conjugation between COO^- and R is possible (Tables 4 and 5). The second process (3) will then occur to an extent dependent on its standard potential.
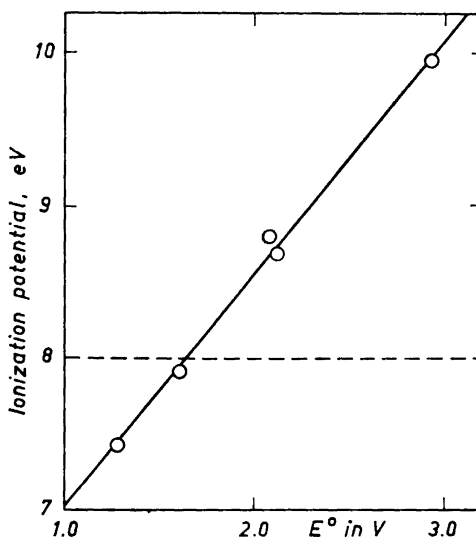
Fig. 2. Standard potential of (3) *versus* ionization potential of R· (see Table 4).

From the method of calculation, it would be expected that $E°$ of (3) is linearly correlated with the electron impact ionization potential, since this parameter is the major contribution to $E°$. Fig. 2 shows that this is the case. (The $E°$ values of Fig. 2 refer to aqueous solution but they differ very little from those calculated for the solvent methanol). This relationship provides a simple means for the prediction of the outcome of a Kolbe synthesis. Ionization potentials are available for a large number of radicals and the list will no doubt be extended rapidly in the future.[36] Fig. 2 has tentatively been divided into two regions, comprising radicals with ionization potentials above or below 8 eV. In the upper region electrode process (3) occurs only to a minor extent and in the lower region to a major extent. Naturally, borderline cases will exist but existing experimental data do not allow a more refined subdivision.

From the Table of ionization potentials in Ref.[36] it is evident that the radicals in the upper region correspond to cases where the Kolbe reaction (formation of $R-R$) can be successfully accomplished. Among these are the primary aliphatic radicals of the general formula $RCH_2·$ (methyl 9.95, ethyl 8.78, propyl 8.33, butyl 8.64, isobutyl 8.35 eV) and the resonance-stabilized radicals of the type $R\dot{C}H-X$ ($\dot{C}H_2CN$ 10.87, $(CH_3)_2$ $\dot{C}-CN$ 9.15 eV). Ionization potentials for $R_2\dot{C}-COOEt$ and $R_2\dot{C}-CONH_2$ are not known but the good (provided disproportionation of the intermediate radicals is excluded) yield of Kolbe product in the electrolysis of substituted malonic half esters [54] and malonamic acids [55] is an indication that these radicals belong to this group.

In the lower region we find radicals where products formed *via* cationic intermediates dominate, *e.g.* secondary and tertiary aliphatic radicals [17,18] (isopropyl 7.90, *t*-butyl 7.42 eV), alicyclic radicals [16,18] (cyclobutyl 7.88, cyclopentyl 7.80, cyclohexyl 7.60 eV), and benzyl or benzhydryl type radicals [56] (benzyl 7.76, benzhydryl 7.32 eV). Evidently a low ionization potential for R·

(less than 8 eV) suggests that the radical formed *via* (5) will be further oxidized to a carbonium ion and the yield of Kolbe product will be low or zero.

In this connection it is interesting to note that a bridgehead carbonium ion is easily formed in the electrolysis of 7,7-dimethylnorbornane-1-carboxylic acid.[17] According to the above reasoning this would imply that the corresponding bridgehead radical has an ionization potential lower than 8 eV. Since it has been shown that the appearance potential of the 1-norbornyl cation in the mass spectrum of 1-norbornyl bromide [57] is abnormally high (10.66 eV, to be compared with that of the *t*-butyl cation, 9.6 eV), this would indicate that the high value should be attributed to a high bridgehead carbon-halogen dissociation energy, *i.e.* the 1-norbornyl radical must be highly strained.

It should be mentioned that this reasoning is independent of the mechanism of the first step. If we for a moment assume that (1) is the primary reaction there will nevertheless be a production of R· very near the anode (say, within a layer of 10 Å thickness), since the decarboxylation process is a very rapid reaction for aliphatic acyloxy radicals (*e.g.*, for the acetoxy radical the rate constant is of the order 10^9 sec^{-1}). However, for reasons given above, the primary step (5) appears more probable.

It has frequently been considered as a proof of the intermediate existence of acyloxy radicals that the electrolysis of a salt of a carboxylic acid in the presence of an unsaturated compound gives an acyloxy derivative of this compound.[56,58-61] Thus, electrolysis of acetate ion in glacial acetic acid with naphthalene [56] or anisole [58] present gives α-acetoxynaphthol and o-acetoxyanisole, respectively, and this was interpreted as an attack of the acetoxy radical upon the aromatic compound. This interpretation is almost certainly not correct, since aromatic systems are known[47] to be oxidized at considerably lower anode potentials according to equation (26)

$$ArH \rightarrow ArH^+ + e \qquad (26)$$

i.e., one electron is removed from the h.o.m.o. In aqueous suspension naphthalene is converted into α-naphthol upon anodic oxidation,[62] which would correspond to the formation of α-acetoxynaphthol in glacial acetic acid.

In conclusion, the mechanism of the Kolbe synthesis conforms to the general mechanism for organic electrode processes. Dependent on its ionization potential, the intermediate radical R· will give the Kolbe product R—R (and other products formed *via* radical reaction paths) or undergo a second anode reaction with the formation of a carbonium ion R$^+$. The latter process appears to be favored for radicals with ionization potentials lower than about 8 eV.

LCAO—MO calculations. Energy levels of the carboxylate ions were calculated by the LCAO—MO method described by Sandström.[63]

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