ELECTRODE KINETIC ASPECTS OF THE KOLBE REACTION

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I. GENERAL INTRODUCTION

Faraday, in 1834, was the first to report electrochemical production of a gas now known as ethane, during electrolysis of aqueous acetate solutions (55). This observation was investigated in more detail by Kolbe in 1849, whence the name of the reaction originated (105). The Kolbe reaction,[1] in general, refers to anodic oxidation of a carboxylate structure with subsequent decarboxylation and coupling to yield a hydrocarbon or a substituted derivative corresponding to the alkyl function in the carboxylate reactant. The best known example is the reaction of acetate which may be represented in terms of the over-all process as

$$2CH_3COO^- \longrightarrow C_2H_6 + 2CO_2 + 2e$$

Many variations of this reaction involving substituted carboxylate structures have been reported, and the general phenomenology (1, 13, 48, 56, 88, 109, 150, 152, 158, 160, 168, 169, 174) of this reaction, based on mainly empirical approaches, has been well established from the point of view of synthetic organic chemistry. The production of hydrocarbons from *mixtures* of aliphatic carboxylates was performed by Wurtz. Such studies have already been extensively discussed and reviewed (13, 168, 169) in the literature and are outside the scope of this review.

In the present review, comparatively recent work on the Kolbe reaction will be stressed, with considerable emphasis on the elucidation of its mechanisms by fundamental studies involving an examination of energetics and electrochemical kinetics of various elementary consecutive events that constitute the over-all Kolbe reaction. Most of the discussion of actual examples of the Kolbe reaction will be restricted to the simplest cases only, since from an electrode kinetic point of view meaningful mechanistic conclusions can, at the present time, only be reached when the number of possible pathways in a reaction is minimized; *i.e.*, conditions are chosen so that side reactions occur to the least extent. The present treatment is thus aimed at considering in detail the most important aspects of the problem for conditions where the results of electrochemical techniques can be regarded as significant. The involvement of a plurality of mechanisms has been implied above; thus, in general, it will not be expected that a single mechanism can be assigned but rather that mechanisms must be considered specifically for each type of electrode metal used or each type of solution investigated.

No discussion of the anodic oxidation of formate ions or of formic acid will be attempted here; although these reactions are superficially similar to the Kolbe reaction (26, 134) in that decarboxylation occurs, the over-all process is, however

$$HCOO^- \longrightarrow CO_2 + H^+ + 2e$$
$$(\text{or } HCOOH \longrightarrow CO_2 + 2H^+ + 2e)$$

The coupled Kolbe analog "H_2" is not formed owing to the facile oxidation of H to protons at noble metal anodes. Basically, therefore, the problems involved in the two reactions are different and there is independent evidence that direct chemical catalytic decomposition of HCOOH also occurs at Pt electrodes (20). In this review, severe restrictions will also be put on the extent to which side reactions and their mechanisms will be discussed. Only in cases where these lead to some further insight into the mechanism of the Kolbe coupling reaction itself will these cases be examined in any detail. For the benefit of any readers who may be specialists in organic chemistry rather than in electrochemistry, some elementary definitions of certain terms which occur frequently in our discussion have been given in the text as they appear; two appendices are also included giving some further but brief details of certain matters which are important in a number of sections in our review.

II. APPROACHES TO THE ELUCIDATION OF THE MECHANISM OF THE KOLBE REACTION

The Kolbe reaction is an organic reaction proceeding on an oxidizing electrode, *i.e.*, an anode. Hitherto, most mechanistic studies on this reaction have understandably involved predominantly either organic chemical approaches or investigations in which the basic nature of the electrodic oxidation processes occurring have been explored.

A. ORGANIC CHEMICAL APPROACHES

In these approaches to the elucidation of the mechanism of the Kolbe reaction, or for any other electroorganic reaction for that matter, an attempt is usually made to obtain information by the following types of experiment.

1. *Products of Electrolysis*
(54, 89, 90, 101, 120, 128, 136)

The characterization of reaction products in modern work (25, 42, 70, 151) is usually carried out by vapor-phase chromatography, mass spectrometry, or some other similar technique. Coulombic yield studies must also be carried out to estimate quantitatively the relative ratios of major products in relation to the number of faradays of charge passed.

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[1] Here, the term Kolbe reaction refers to the Kolbe *electrosynthesis* of hydrocarbons and not to a chemical synthesis of aromatic carboxylic acids (106), also discovered by Kolbe and known by this name. What is known as ethane today, Kolbe (1849) called "methyl" with the formula "C_2H_3" (105); Schorlemmer (1864) subsequently identified it as C_2H_6 and called it "ethane" (124). Kolbe had attempted to prepared the radical "methyl" by electrolysis; the formula "C_2H_3" arose because C = 6 was assumed and the fact that ethane was "dimethyl" was not at the time realized. "Methyl" was also prepared by Kolbe from acetonitrile by the action of potassium; the product was, of course, ethane.

2. Substitution Reactions (1, 12, 37, 39, 45, 47, 49, 57–60, 76, 90, 91, 95, 96, 112, 130, 131, 137, 140, 144–146, 169, 172, 173)

Some suitable organic substrates can be added in the anode compartment of a cell in which, for example, the electrolysis of a potassium acetate–glacial acetic acid mixture is occurring. The identity of the resulting derivatives of the organic substrate, now substituted by the reactive intermediates involved in the Kolbe reaction, can be established by conventional procedures, and hence the nature of these intermediates may be deduced.

It may be noted that evidence from substitution reactions regarding the identity of intermediates that may be formed in the Kolbe reaction is not always unambiguous. For example, if an organic substrate molecule A is acetoxylated when subjected to electrolysis with acetate–acetic acid solution, it may perhaps be suspected that acetoxyl radicals are formed during the electrolysis and are responsible for substitution in A. However, alternatively, A may be oxidized to A^+ on the anode (*cf.* ref 49) and then may react with the anions (*i.e.*, acetate ions) in the solution to give acetoxylated A. Sometimes more complicated pathways may be involved (62, 129) and clear-cut conclusions may be difficult to make. However, in cases where methylations have been observed (*e.g.*, of trinitrotoluene), this seems to be a strong indication of the involvement of methyl radicals, but antecedent radicals such as $RCOO\cdot$ are certainly not excluded by this observation. The yield of methylated substrate product will depend, in general, on the relative values of the rate constants for methyl radical recombination and methylation of the substrate; for the latter process, diffusion of the substrate to the electrode surface could also be a limiting factor. Initiation of vinyl polymerizations in the presence of an electrode at which the Kolbe reaction is occurring is another indirect indication of the participation of radicals in the Kolbe reaction mechanism.

Evidence for the involvement of acetoxy radicals in the Kolbe reaction, argued on the basis of the observed production of acetoxy derivatives of various substrate molecules such as naphthalene or anisole, has been criticized by Eberson and Nyberg (49). These workers showed by polarographic studies at a rotating Pt anode in acetic acid–0.5 *M* sodium acetate solution that with a number of aromatic substrate molecules cations of the substrate can be formed which react with the acetate *ion* to give the acetoxylated product. The implication of these authors that production of the $CH_3COO\cdot$ radical would not occur until above 2.0 v is, however, incorrect since the reversible potential for the Kolbe reaction is much lower (see section V.A.2) than this figure and $CH_3COO\cdot$ radicals could be formed (albeit at a small rate) at potentials *below* the potential required for anodic formation of substrate cations. At the practical potentials involved in carrying out a Kolbe type of electrolysis at a moderate rate ($>10^{-2}$ amp cm^{-2}), the proposals of Eberson and Nyberg will, however, be applicable. Homogeneously (12, 96), the lifetime of the acetoxy radical is very short, but its behavior and properties under such conditions must not be confused with its chemical reactivity when in a chemisorbed condition (see sections III.A.2 and V.A.3). Further evidence for the alternative substrate ionization pathway in electrolysis of acetic acid–acetate solutions has been given by Salzberg and co-workers (112, 137) and by Ross, Finkelstein, and Petersen (133) who found the oxidation potential required for electrolysis at appreciable rates was sharply lowered in the presence of the organic substrate. Again, it must be borne in mind when interpreting such observations that such effects could arise for kinetic reasons if decarboxylation of $CH_3COO\cdot$ radicals were a slow process and addition of the organic substrate simply provided a new depolarization pathway alternative to the succeeding desorption steps (164)

$$\begin{tikzcd}
CH_3COO\cdot \arrow[r] & CH_3\cdot + CO_2 \arrow[d] \\
 & 0.5C_2H_6
\end{tikzcd}$$

or

$$CH_3COO\cdot + CH_3COO^- \longrightarrow C_2H_6 + 2CO_2 + e$$

necessary for completion of the over-all Kolbe reaction. Thus, indirect chemical evidence for involvement of carboxy *radical* species is available in certain other cases; *e.g.*, in the electrolysis of 3,3-diphenylacrylic acid, a cyclization product, 4-phenylcoumarin results, which must arise from a carboxy radical corresponding to the original acid (103). This reaction is analogous to the electrochemical formation of 4-phenyl-3,4-dihydrocoumarin from 3,3-diphenylpropanoic acid, as pointed out by Koehl (103). These observations complement the evidence arising from acetoxylation reactions with various substrates at electrodes where the Kolbe reaction is taking place (11).

General conclusions probably cannot be made except in the cases of the simple aliphatic carboxylic acids. However, even if acetoxylation of certain easily oxidizable substrates does occur by an ionic mechanism, this only invalidates the use of such a method as an indicator for acetoxyl radicals in the acetate Kolbe reaction and does not disprove in any way the involvement of such radicals in the Kolbe reaction sequence itself.

3. Isotopic Tracer Studies (19, 87, 100, 141)

Clusius and co-workers (19, 141) carried out investigations on the mechanisms of some side reactions involved in the Kolbe electrolysis. They conducted electrolysis of acetates and deuterioacetates in deuterium oxide and water, respectively. It was found that the isotopic composition of both ethane (formed at high potentials) and methane (formed at lower potentials) depends on the isotopic substitution of the acetate ion only, and not on that of the solvent. It was concluded that methyl radicals are formed and that these either dimerize to give ethane, or, when present in low concentrations, abstract hydrogen from an acetate ion or another methyl radical (and *not* from the solvent) to give methane. These results imply (a) that the methyl radicals are never free in the solution and (b) that the abstraction of H (or D) occurs by a catalytic surface reaction between the methyl radicals and other methyl radicals (or acetoxyl radicals) adsorbed on the electrode in preference to reaction with solvent H_2O or D_2O in the double layer at the interface or in the bulk.

From the type of information obtained in sections 1–3 above, conclusions regarding the type of "mechanism" involved can sometimes be made. This approach has been adopted in much of the earlier work and also in some recent investigations.

B. ELECTROCHEMICAL APPROACHES

Here a variety of *complementary* steady-state and non-steady-state methods are available (21, 25, 26, 31–35, 42, 64, 66, 70, 71, 87, 116, 162–164, 173). Their application yields information on (a) the basic nature of the charge-transfer process; (b) associated events in the Kolbe reaction which can occur either prior or subsequent to the charge-transfer step at the metal–solution interface; and (c) relative values of the electrochemical rate constants for various reaction steps. The various types of quantitative information which these approaches yield are discussed below (section IV) and are relevant to the deduction of the following matters: (a) the reaction pathway which usually involves two or more consecutive processes; (b) the rate-determining stage (rds) within the plausible reaction pathway; (c) nature of any parallel reactions, *i.e.*, alternative mechanisms and/or side reactions; (d) complications that arise due to concomitant oxidation of water in the aqueous medium with resultant formation of oxygen-containing species (surface oxides) at the metal surface; (e) presence of adsorbed intermediates at the electrode interface.

C. RELATIVE ASSESSMENT OF THE TWO APPROACHES

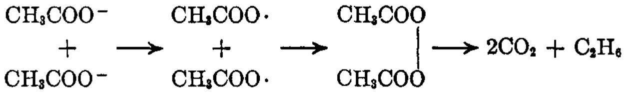
It is obvious from sections A and B above that the organic chemical and the electrochemical approaches are complementary in nature and both are essential for a complete understanding of the reaction mechanism. However, the organic chemical approaches determine only the principal reaction pathway(s) and establish the general phenomenology of the reaction; the fundamental aspects of the charge-transfer process and kinetically related succeeding steps involved in the reaction can usually only be understood by application of electrochemical approaches to systems which are sufficiently simple from an organic chemical viewpoint that meaningful conclusions can be drawn.

III. PROPOSED THEORIES OF THE KOLBE REACTION

During the past several decades, various theories have been put forward for the mechanism of the Kolbe reaction and will be summarized below.

A. ACYL PEROXIDE THEORY

This was originally proposed by Schall (140) and subsequently developed by Fichter (56–58). For the case of the Kolbe reaction at platinum in acetate solutions, these investigators proposed that the acetate ions were discharged at the anode, and the resulting acetoxyl radicals reacted to form diacetyl peroxide which then decomposed to form alkyl radicals and thence the hydrocarbon. Their mechanism (58) was suggested by the fact that diacetyl peroxide was known to undergo thermal decomposition homogeneously to give (in part) a hydrocarbon and carbon dioxide. The reaction pathway involved here may be represented by



$$\begin{matrix} \mathrm{CH_3COO^-} & & \mathrm{CH_3COO\cdot} & & \mathrm{CH_3COO} & \\ + & \longrightarrow & + & \longrightarrow & | & \longrightarrow 2\mathrm{CO_2} + \mathrm{C_2H_6} \\ \mathrm{CH_3COO^-} & & \mathrm{CH_3COO\cdot} & & \mathrm{CH_3COO} & \end{matrix}$$

No adsorption of any intermediate species at the surface was recognized.

If this mechanism were valid, it would be expected that diacetyl peroxide would be detectable under normal conditions of electrolysis; positive results were obtained only under very special experimental conditions (low temperatures and streaming of the electrolyte) when diacetyl peroxide was detected in very small amounts (59, 60). Even under these circumstances, it cannot be concluded that diacetyl peroxide is a true intermediate in the consecutive series of reactions which are involved and not a side product arising from the rather special conditions used. This, among other observations, is a major objection to this theory.

A second, but less serious, objection is that in the homogeneous decomposition of a peroxide, such as propionyl peroxide, recent work by Eberson has shown that the relative yields of C_2H_6 and n-C_4H_{10} are different from those in the Kolbe reaction with propionic acid.

B. HYDROGEN PEROXIDE THEORY

This theory was proposed by Glasstone and Hickling (88–91). According to these authors, in the electrolysis of aqueous acetate solutions, hydrogen peroxide is first formed by immediate irreversible combination of hydroxyl radicals preceded by the discharge process

$$\mathrm{OH^-} \longrightarrow \mathrm{OH\cdot} + \mathrm{e}$$

The OH· radicals thus formed were regarded as combining to give H_2O_2, *i.e.*

$$2OH\cdot \longrightarrow H_2O_2$$

The authors did not, however, explicitly specify whether the combination of two OH· radicals is a homogeneous or a heterogenous process. The hydrogen peroxide thus formed then reacts with the acetate ions to form acetate radicals. These then combine, possibly with the intermediate formation of diacetyl peroxide, to yield ethane and carbon dioxide according to the scheme

$$2CH_3COO^- + H_2O_2 \xrightarrow{\text{homogeneously}} 2CH_3COO\cdot + 2OH^-$$

followed by

$$2CH_3COO\cdot \xrightarrow{\text{homogeneously}} (CH_3COO)_2 \xrightarrow{\text{homogeneously}} CH_3CH_3 + 2CO_2$$

This mechanism has been subject to numerous criticisms, the most serious of which are (a) that addition of concentrated hydrogen peroxide to acetate solutions produces only trace amounts of hydrocarbon (88–91); (b) that attempts to detect even trace amounts of hydrogen peroxide during and following Kolbe electrosynthesis have not been successful (1,169); (c) that this mechanism also fails to account for the fact that the Kolbe synthesis takes place with the best efficiencies in *nonaqueous* media where H_2O_2 could not be involved (25, 31, 34, 54, 101, 162, 169).

C. THE FREE-RADICAL THEORY

1. Origin of Radicals

This was originally proposed by Crum-Brown and Walker (an "incipient" free-radical theory) (39) and developed by Walker and co-workers (143, 144, 166). The important steps in the proposed mechanisms are the direct electrochemical oxidation of the carboxylate ion and the subsequent decomposition of the radicals formed. The consecutive steps in the reaction may be written as shown below and indicate the origin of the radicals.

$$2RCOO^- \longrightarrow 2RCOO\cdot + 2e \text{ (presumably in two separate steps)}$$
$$2RCOO\cdot \longrightarrow 2R\cdot + 2CO_2 \text{ (in two separate steps)}$$
$$R\cdot + R\cdot \longrightarrow R{-}R$$

Although it was not realized or mentioned in early discussions on this theory, the presumption must be made (*cf.* the case of other electrochemical discharge reactions (122)) that the radicals RCOO· and R· in the above scheme are formed in a specifically adsorbed or chemisorbed state at sites upon the metal electrode surface acting as an electrocatalyst for the reaction. This matter is of some importance in assessing the nature and reactivity of the intermediate species involved in the above steps. If chemisorption is involved, the radical species cannot strictly be referred to as *free* radicals, and indeed if they are adsorbed at transition metal electrodes, their odd-electron character may be effectively diminished and the number of d holes per atom of the electrode surface atoms may then also diminish (*cf.* the cases of H chemisorption and H sorption into palladium) by electron pairing in the interphase (115, 153, 175).

A number of elegant investigations have been reported which tend to favor a free-radical mechanism for the Kolbe reaction. Such studies include the work of (a) Clusius and co-workers who used isotopic tracer techniques (19, 100, 141) (see above); (b) Wilson and Lippincott, who reported kinetic studies (173) (see section V.B.2) of the anodic oxidation of carboxylic acids by a periodic polarization technique (*cf.* the rotating-sector technique for the study of photochemical gas-phase reactions (45)); (c) Fieser, Clapp, and Daudt, who showed that trinitrotoluene can be methylated in the anode compartment during electrolysis of an aqueous solution of acetate (61); (d) various investigators who have demonstrated acetylations and acetoxylations of certain organic substrates during Kolbe electrolyses of simple aliphatic carboxylates (77, 145–147, 169, 171, 172) [however, the substitution reactions mentioned here and in (c) above are not unambiguous (see p 625 and ref 49)]; (e) a number of investigators who have made electrode kinetic approaches (see below) (21, 25, 26, 31–35, 42, 64, 66, 70, 71, 87, 116, 162–164, 173).

2. The Question of Involvement of "Free" or "Adsorbed" Radicals

It is a matter of some general importance in regard to the mechanism of the Kolbe reaction and the associated side reactions to discuss the evidence for participation of truly "free" radicals, on the one hand, or adsorbed radicals, on the other. Thus, it seems to be assumed by a number of workers, particularly those interested in the organic chemistry of the reaction, that *free* radicals may be formed which undergo subsequent reactions in the solution phase.

First, it must be stated that no esr evidence seems yet available in support of the existence, in solution, of "free" radicals formed in the Kolbe reaction. However, this cannot be regarded as definite evidence for their absence, only perhaps for their short lifetime and small steady-state spin density.

From an electrochemical point of view, it is very difficult to imagine an ion-discharge step proceeding at a noble catalytic and adsorbing metal surface without the resulting neutral radical being chemisorbed (122). Considerable direct and indirect evidence for this exists with regard to other ion-discharge processes and quite generally, for exo-energetic adsorption, the free energy of activation for any kinetic pathway of ion discharge will be less for the production of an adsorbed discharged species than for that of a *free* discharged radical species (122); the former process will therefore tend to be kinetically as well as thermodynamically favored. The fact that chemisorbed species cannot always be detected by electrochemical means (as, for example, in the case of H at the mercury cathode in the hydrogen evolution reaction) must not be taken as evidence for their lack of involvement in the reaction, only for the small surface concentration of the radicals in the steady state. In the example mentioned, it is believed that the H atoms are chemisorbed at Hg with an energy of at least 50 kcal mole^{-1} (122). Their small coverage arises simply because the rate constant for H atom recombination is relatively large. The arguments in this paragraph refer specifically to the production by ion discharge of an acyloxy radical of the form RCOO·, adsorbed at a site M upon the metal surface.

In a possible subsequent step of the Kolbe reaction (see section IV.A.2) RCOO· must presumably dissociate to give R· and CO_2. The next question that requires discussion is the fate of the R· radical. At an electrocatalyst interface, it seems improbable that RCOO· formed in an adsorbed condition would not undergo a heterogeneous catalyzed decomposition (*cf.* the decarboxylation of HCOOH on metal catalysts) to give an *adsorbed* R· radical at a neighboring site with release of (initially adsorbed) CO_2. Subsequent recombination would also tend to be catalyzed by the surface, *e.g.*, as in H atom recombination.

Work on optically active carboxylic acids R*COOH, where R* now involves a trifunctional C atom, indicates (*e.g.*, with methylethylacetic acid (167a)) that Kolbe coupling does *not* give an optically active Kolbe dimer R*–R* (40a, 146a, 167a). It has been argued, *e.g.*, by Eberson, that this indicates that the R* radicals become truly free in the solution and recombine with loss of the optically active configuration associated with R*– in the compound. If the reaction were heterogeneous with R* being chemisorbed to the surface (so that R*– effectively retained its asymmetric configuration), it can be argued that an optically active Kolbe dimer would result. While the latter conclusion, if it was indicated experimentally, which is not the case, would be positive evidence for retention of configuration by chemisorption of an R* radical, the absence of such an effect, we believe, does *not* prove that R* radicals are *not* chemisorbed, nor does it indicate that the recombination is not heterogeneous.

The activation energy barrier for "umbrella" inversion of a trigonal radical corresponding to R* must be quite small (*ca.* 2–3 kcal), and at a metal surface loss of configuration may also be catalyzed. Also, in the decarboxylation step, it seems that loss of configuration in R* may well tend to occur without the radical becoming completely free and desorbed into the solution. Finally, the electrode surface at most solid metals is normally quite heterogeneous in the sense of exhibiting many corners, declivities, asperities, and edges, and it is unlikely that an optically active R*–COO· radical would form only the corresponding R*–M chemisorbed species in the same optically active configuration; at some sites R* may adsorb from one direction to the M site, and at other sites from the opposite direction, bearing in mind the microscopically rough nature of real metal surfaces and the thermal librative motions of chemisorbed radicals. This situation is equivalent to a Walden inversion and is illustrated in Figure 1.

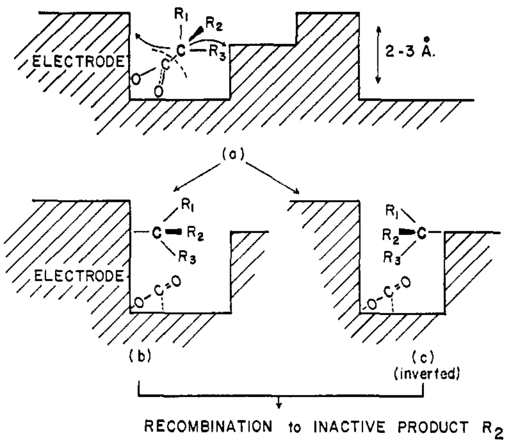


Figure 1.

In formulating such local details of the reaction steps involved, consideration will ultimately have to be given to cooperative aspects of the surface reactions involved, *e.g.*, in decarboxylation, how the dissociation of the R group might be concerted with its adsorption at one site and the adsorption of CO_2 at another site, bearing in mind the presence of excess (adsorbed) solvent molecules. At the moment, the present level of experimental knowledge of such catalytic and electrochemical effects is too inadequate for more than intelligent speculations to be made about the molecular mechanics of such steps.

Other indirect electrochemical evidence against the formation and homogeneous recombination of R radicals is as follows: (a) Fioshin and Vasil'ev (66) have found that the rate of formation of C_2H_6 in the acetate Kolbe reaction is independent of rotation speed of a rotating platinum electrode (if radicals were spun off into the solution phase, their recombination would tend to be a less efficient process the more they were dispersed into the solution away from the boundary layer near the electrode); (b) Fleischmann and co-workers (70) have found that with increasing frequency in pulsed electrolysis the Kolbe dimerization becomes less favored than the Hofer–Moest oxidation (see section V.B.2). If the dimerization was an homogeneous process among "free" radicals, it is difficult to see how the observed result could arise since the origin of the effect is regarded as being associated with competitive processes of oxidation and recombination at the surface of the electrode

(70). Here, the relative value of the rate constants will be involved, as well as the reaction order (173).

If the recombination occurred in solution among free radicals, it might be expected that the yield of hydrocarbon RH in relation to the yield of coupled Kolbe R_2 might be greater in the pure carboxylic acid solution, RCOOH (*e.g.*, glacial acetic acid), than in excess water, due to favored conditions for homogeneous H atom abstraction from "R" in RCOOH. This is not usually the case experimentally where the best yields of R_2 are obtained in nonaqueous media. However, in suitable nonaqueous solvents, free $R\cdot$ radicals might be stabilized sufficiently if $R\cdot$ is a large species.

The ratio of disproportionation to recombination products in homogeneous radical–radical reactions is well known (169a) and depends on the type of radicals involved. For simple aliphatic radicals such as $C_2H_5\cdot$ and n-$C_3H_7\cdot$, this ratio is 0.12–0.14 and 0.15–0.17, respectively. In the Kolbe reaction, Fioshin and Vasil'ev (66), in agreement with earlier work, have found the ratio of the yields of olefin corresponding to R and paraffinic hydrocarbon (*i.e.*, $R_2 + RH$) as follows: from propionic acid ($R = C_2H_5$) 8.2, and from n-butyric acid 3.9. These yield ratios lead to ratios between disproportionation and recombination products which are respectively 100 and 30 times larger than the expected ratios for homogeneous disproportionation and recombination processes. These results hence constitute strong evidence against any appreciable participation of homogeneous radical–radical reactions. If the reactions proceeded catalytically, it is likely that different activation energies for the two types of processes would be involved owing to the chemisorption of the $R\cdot$ radicals, so that relative yields of recombination and disproportionation products substantially different from the yields arising in the corresponding homogeneous processes (which have zero or low activation energy in the gas phase) might be expected.

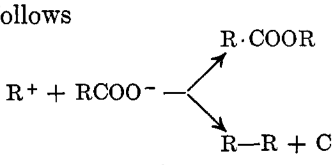
In Table I, a comparitive summary is given of the evidence for free and adsorbed radicals.

D. CARBONIUM ION THEORIES

There is evidence that "carbonium" ion intermediates are sometimes produced by more extensive anodic oxidation of $RCOO^-$ as follows (37, 45, 49, 130, 167).

$$RCOO^- \xrightarrow{-e} RCOO\cdot \xrightarrow{-CO_2} R\cdot \xrightarrow{-e} R^+$$

The carbonium ion R^+ may perhaps then react with $RCOO^-$ as follows



$$R^+ + RCOO^- \longrightarrow \begin{cases} R\cdot COOR \\ R{-}R + CO_2 \end{cases}$$

or with water to give alcohols.

These mechanisms are probably not involved in the Kolbe reaction itself for the simple reason that stable carbonium ions have been reported only in those cases where the Kolbe coupling usually fails (63, 111, 165). This pathway may thus be important only in reactions *parallel* (81) to the Kolbe reaction (see section VI.B), resulting in a variety of side products, *e.g.*, as in the Hofer–Moest reaction leading to alcohols (*e.g.*, in the case (169) of acetate at gold anodes in aqueous medium) or in other side reactions leading to esters or to rearranged products. The evidence in special cases, *e.g.*, the complex carboxylic acids considered by Corey (37), is nevertheless good that carbonium ions can be formed at anodes at high potentials. In these cases, again, true Kolbe products are not, in fact, formed. Carbonium ion production will obviously be a possible pathway (see section VI.B) when the acid or R has a low ionization potential and the resulting ion can be stabilized by solvation. The relative predominance of carbonium ion products will depend on the relative rates of the ion-producing pathway and the radical coupling pathway (see section VI.B).

IV. ELECTROCHEMICAL STUDIES ON THE KOLBE REACTION

Electrochemical studies are usually concerned with understanding the nature of the processes involved in charge transfer across the metal–solution interface and the relation of these processes to (a) the reaction mechanism as a whole and (b) to the involvement of any intermediate species. These approaches may be classified as follows.

A. STEADY-STATE CURRENT–POTENTIAL RELATIONS

In this kind of approach, the relation between steady-state rates (*i.e.*, current–densities i) and the corresponding electrode potentials is examined [electrode potential controls (see Appendix I) the height of the activation energy barrier for the reaction]. On plotting the electrode potential V against log (rate), usually a linear region is obtained for the predominant over-all reaction in a given potential range. This well-known straight-line behavior is called the Tafel region and the slope of this line, $dV/d \ln i$, is called the Tafel slope, b (21, 155). The Tafel relation can be regarded as a form of the Arrhenius equation.

Tafel slopes may be deduced theoretically for various conditions of surface coverage of the electrode by reaction intermediates and can be shown to be characteristic of the reaction mechanism in a number of cases (6, 7, 21, 22, 25, 78, 119, 122) and under certain limiting conditions (6, 7, 22, 25, 122).

1. *Theoretical Analysis for Kinetic Criteria of Mechanisms*

In general, most electrochemical reactions, except perhaps one-electron ionic redox process, proceed by at

Table I

Comparative Evidence for Free or Adsorbed Radicals

Method and exptl facts	For "free" radicals	For adsorbed radicals
1. Use of optically active acid RCOOH	Coupled product R_2 is optically inactive (racemic or *meso* ?)	Optically active configuration may have become lost upon decarboxylation and readsorption of radical R at various surface sites, as expected at a nonsmooth catalytic metal surface
2. Nature of discharge process	Free RCOO· unlikely to be formed since the metal site participates in discharge event	Kinetically favored pathway will tend to be the one in which the discharged ion is chemisorbed as in H_2 evolution, etc.
3. Relative yields of recombination and disproportionation products	Should be similar to ratio found in gas-phase reaction—not found to be the case experimentally	Disproportionation products formed in far too great a relative yield to be consistent with homogeneous radical–radical reactions
4. Isotopic tracer experiments involving D_2O and CD_3COOH	Results seem to be inconsistent with homogeneous free-radical reaction, but evidence regarding coupling is not given by this method	Reaction between adsorbed species indicated, at least with regard to side production of lower hydrocarbons
5. Rotating disk electrode study	Rate of production of ethane might be expected to depend on rotation rate—not observed	Rate of production of ethane independent of rotation rate—observed
6. Electron spin resonance	No conclusive result available	No conclusive result available
7. Analogy to other reactions	No electrochemical indications that molecular fragments are free	Indirect proof of adsorption of molecular fragments in electrochemical hydrocarbon, formate, methanol oxidation is well accepted; coverage by fragments can be determined
8. ^{14}C-labeling experiments	No evidence given by this method	$^{14}C_1$ and $^{14}C_2$ acetate is chemisorbed on Pt—direct determination by ^{14}C β count at thin metal electrode surfaces; $^{14}C_2$ indicates adsorption process is slow and irreversible
9. Alkylation and acetoxylation of substrates in presence of an electrode at which Kolbe reaction is proceeding	Ambiguous	Ambiguous; reactions could occur through adsorbed species, or homogeneously, or in some cases by oxidation of the substrate itself
10. Pulsed electrolysis studies	If radicals have left surface, recombination cannot be competitive with further surface oxidation processes, *e.g.*, to give R^+, ROH, etc.; "free" radicals not supported	Competitive reactions involving adsorbed species can explain effect of frequency on relative yields of products

least two consecutive steps. It is unlikely that the Kolbe reaction, which involves two ions, decarboxylation, coupling, and transfer of two electrons for one act of the over-all reaction, takes place in one step; it must proceed through a sequence of consecutive elementary processes. A brief discussion of such a scheme, together with its kinetic consequences based on the considerations first developed quantitatively by Conway and Dzieciuch is presented below (25).

In the over-all Kolbe reaction

$$2RCOO^- \longrightarrow R{-}R + 2CO_2 + e \qquad (A)$$

the following sequence of consecutive elementary steps[2] may be envisaged

$$RCOO^- \longrightarrow RCOO\cdot(M) + e \qquad (B)$$

$$RCOO\cdot(M) \longrightarrow R\cdot(M) + CO_2 \qquad (C)$$

involving adsorption at a site M on the metal surface, followed by

$$R\cdot(M) + R\cdot(M) \longrightarrow R{-}R \qquad (D)$$

or

$$RCOO\cdot(M) + RCOO\cdot(M) \longrightarrow R{-}R + 2CO_2 \qquad (D')$$

or

$$RCOO\cdot(M) + R\cdot(M) \longrightarrow R{-}R + CO_2 \qquad (D'')$$

and alternatively

$$RCOO\cdot(M) + RCOO^- \longrightarrow R{-}R + 2CO_2 + e \qquad (E)$$

or

---

(2) A number of other side reactions such as formation of RH by H abstraction or formation of esters by reaction of R· with RCOO· may also occur (*cf.* the carbonium ion pathway) (169). However, in the present discussion, only the simplest case where R is CH_3 or CF_3 will be considered. Exhaustive fluorination of the alkyl group minimizes the abstraction processes and any parallel oxidations of a more drastic nature.

$$\mathrm{R\cdot\ (M) + RCOO^- \longrightarrow R{-}R + CO_2 + e} \qquad (\mathrm{E}')$$

Step B in the above scheme is the initial discharge of the carboxylate ion at the electrode surface to give an adsorbed[3] RCOO· radical; this step is usually referred to as the "discharge step;" Step C is an heterogeneous catalyzed "chemical step" in which R· is produced from RCOO· on the electrode surface; this step is a chemical one because no charge transfer across the metal–solution interface is involved. Steps D, D′, and D″ are kinetically (but not chemically) equivalent since each one is a "recombination step;" *i.e.*, it involves recombination of two radicals, the identity of which must be established from other evidence. Steps E and E′ are again kinetically indistinguishable; E or E′ will be referred to as "electrochemical desorption" steps (or "radical-ion" reactions in the terminology of Parsons (123)).

In the over-all Kolbe reaction, carboxylate radicals must be produced in a "discharge step" and, in some cases, decompose heterogeneously in a subsequent "chemical step" to give R·. For the production of the Kolbe products, *i.e.*, R–R + CO_2, the radicals thus formed on the electrode must be removed from it by coupling through either a "recombination step" (D or D′ or D″) or an "electrochemical desorption step" (E or E′).

For simplicity of discussion, the kinetically indistinguishable steps in the above scheme will be ignored for the time being. The above scheme is then reduced to

$$\mathrm{RCOO^- \longrightarrow RCOO\cdot\ (M) + e} \qquad (\mathrm{B})$$

$$\mathrm{RCOO\cdot\ (M) \longrightarrow R\cdot\ (M) + CO_2} \qquad (\mathrm{C})$$

$$\mathrm{R\cdot\ (M) + R\cdot\ (M) \longrightarrow R{-}R} \qquad (\mathrm{D})$$

or

$$\mathrm{R\cdot\ (M) + RCOO^- \longrightarrow R{-}R + CO_2 + e} \qquad (\mathrm{E}')$$

The problem next is to examine the kinetic consequences in terms of Tafel slopes $dV/d\ln i$ and coverage effects for the possibility of each one of the above steps being the rate-determining stage (rds) in the above sequence of consecutive processes constituting the over-all Kolbe reaction.

The derivation of Tafel slopes for this scheme has been discussed in the literature (25); the procedures for derivation of Tafel slopes for any general case have been reviewed (6, 7, 21, 22, 78, 119, 122), and the theoretically deduced values are summarized in Table II.

The Tafel slopes given in Table II are the limiting values derived by assuming Langmuir conditions, *i.e.*, when interaction and/or heterogeneity effects in the adsorption of intermediates are absent and the adsorption equilibrium is characterized by a coverage-independent equilibrium constant. The corresponding Tafel slopes, under conditions where coverage dependence of activation energies must be included in the kinetic equations (27, 159), have not been included in the table, the reason being that the values of Tafel slopes experimentally obtained for the Kolbe reaction are in general $>2RT/F$ and are hence beyond the range of applicability of the treatment for Temkin conditions[4] which tends to give b values less than $2RT/F$.

TABLE II

Rds	Naperian Tafel slope	Limiting conditions
B	$2RT/F$	Rate constants for the following steps relatively large so that $\Theta_{\mathrm{RCOO}\cdot} \rightarrow 0$
C	(a) RT/F	(a) $\Theta_{\mathrm{RCOO}\cdot} = f(V)$
	(b) Limiting current	(b) $\Theta_{\mathrm{RCOO}\cdot} \rightarrow 1$ and potential independent
D	(a) $RT/2F$	(a) B and C in quasi-equilibrium and coverage by R· potential dependent
	(b) Limiting current	(b) $\Theta_{\mathrm{R}\cdot} \rightarrow 1$ and potential independent
E′	(a) $2RT/F$	(a) B and C in quasi-equilibrium and $\Theta_{\mathrm{R}\cdot} \rightarrow 1$ and potential independent
	(b) $\frac{2}{3}(RT/F)$	(b) $\Theta_{\mathrm{R}\cdot}$ potential dependent

It is to be noted that an important consequence of the above discussion in terms of effects connected with coverage of the electrode is as follows.

If the discharge step B were rate determining (*i.e.*, if it has the smallest rate constant), all the subsequent steps (*i.e.*, the steps involved in the removal of the discharged RCOO·) will tend to have appreciably higher rate constants, with coverage of the electrode by RCOO· consequently approaching a small value. However, this does not imply that the electrode may not be covered by some species adsorbed by the electrode from the ambient solution by a chemisorption process. If any step other than the discharge step B were rate determining, conditions may arise in which partial or complete coverage of the electrode can be observed in the complementary transient studies (to be discussed below), assuming that the adsorbed species is electroactive, *i.e.*, if it can undergo a more or less reversible electron-transfer reaction and is therefore susceptible to facile reduction in a cathodic transient.

In order to explain Tafel slopes greater than $(2RT/F)$ (especially in the post-transition region; see footnote 8 in section IV.B.3.d) as indeed are experimentally observed in the Kolbe reaction, a model

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[3] This factor of adsorption of the intermediate species is one that has not always been appreciated by some workers who have studied the Kolbe reaction (46, 138). Thus, the reactivity of such species when adsorbed at a metal electrode surface must not be confused with the supposed high reactivity of such species in homogeneous solution or in the gas phase (32) (see also the discussion in sections III.D and V.A.3).

[4] A procedure for derivation of anomalously high Tafel slopes under Temkin conditions has been recently proposed (69). However, this method involves an assumption that in the steady state, the rate of back-reactions of all steps prior to the rds can be neglected. It appears, however, doubtful if such an assumption is acceptable and there is no experimental basis for it.

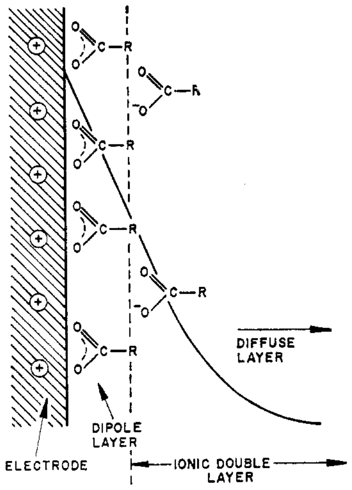

Figure 2.—Schematic representation of "metal–solution" potential drop at an electrode with a dipole barrier-layer type of film of adsorbed intermediates (after Conway and Dzieciuch (25) and *cf.* ref 113 and 114).

involving a dipole barrier-layer film of adsorbed species on the electrode may be involved (Figure 2) (25). If thin and moderately conducting barrier-layer films, or a dipole monolayer, are involved at the interface, part of the total metal–solution potential drop will fall across this film and part across the ionic double layer, through which the ion discharge takes place. This latter process then occurs with an effective symmetry factor (referred to the total metal–solution potential difference; see Appendix I) which can be less than 0.5 and may be as low as 0.25–0.2 depending on the properties of the electrode material and the barrier film (92, 113, 114).

The barrier-layer film model as a basis for explanation of Tafel slopes greater than $(2RT/F)$ was originally suggested for processes occurring at thick oxide films (100–1000 A) (92, 114). The model, however, has been successfully applied to explain high Tafel slopes on electrodes which can be satisfactorily assumed to be covered only with moderately or very thin films (25, 31, 113, 162–164). In such cases, the barrier layer becomes limitingly an oriented dipole monolayer.

Some alternative explanations of high Tafel slopes (*i.e.*, $\gg(2RT/F)$ which have been considered must also be mentioned. Depending on barrier dimensions, slopes up to $5RT/F$ have been theoretically predicted by invoking proton tunneling (18), which is obviously inapplicable to the type of reaction under consideration here (164). High Tafel slopes may also arise on account of potential-dependent impurity adsorption (9). At the high anodic potentials involved in the Kolbe reaction, however, it is unlikely that an organic impurity would not be oxidized off (72, 82, 164). Another explanation involves an unrigorous derivation based on an assumption that in the steady state the rates of the back-reactions for all steps prior to the rds can be neglected (69, 70). For general kinetic reasons it seems, however, doubtful if such an assumption is realistic (164). Also, it involves an experimentally unlikely assumption of linear dependence of coverage on potential (in the Kolbe region) which the results do not substantiate (164). Recently it has been suggested that anomalously high Tafel slopes arise in the case of the Kolbe reaction owing to specific anion adsorption on the electrode (66, 87). However, the relatively high Tafel slopes (~0.2–0.25 v) that are usually observed in case of the Kolbe reaction are probably beyond the values that might be expected on the basis of anion adsorption effects (31). The high Tafel slopes arise also in mineral acid (*e.g.*, H_2SO_4) solutions of carboxylic acids where the free organic ion concentration is very low so that organic ion adsorption would not be involved under such conditions.

High Tafel slopes may also arise (*cf.* ref 41) on account of an unsymmetrical activation energy barrier at the bare metal–solution interface; *i.e.*, the intrinsic symmetry factor β for the charge transfer would be appreciably less than 0.5. This situation seems unlikely in the present case for the following reasons (162, 164): (a) theoretically, a value of β close to 0.5 is expected for most reactions as may be deduced by consideration of potential energy barriers for discharge processes (21); (b) for widely different types of acids and bases, Brønsted's "α" or "β" coefficients, which have a significance closely analogous to that of β, are often (but not always) near to 0.5 (20); (c) the possibility that a low value[5] of β might arise for some intrinsic geometrical or other special reasons in the course of discharge of bulky CH_3COO^- is unlikely because a more normal value of β is actually observed for the acetate Kolbe reaction in completely anhydrous solution (34).

Hence the explanation of high Tafel slopes on the basis of a dipole barrier-layer film model seems somewhat more satisfactory than the alternative proposals. However, the matter still rests on an empirical basis, requiring more quantitative evaluation.

2. Experimental Evaluation of Kinetic Parameters from Controlled-Potential and Controlled-Current Measurements

Current–potential relationships (*i.e.* rate–activation energy relations) have usually been obtained under two kinds of steady-state experimental conditions.

a. Galvanostatic

Here current is controlled as the independent variable, and corresponding values of potential at given

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(5) The fact that at potentials above 2.5 v, the Tafel slope suddenly decreases from a high value to a lower one (but still >120 mv) on platinum in aqueous acetate solutions (162, 164) also indicates that the high β values do not originate from a low value of the conventional β coefficient since the latter, if it varied at all from 0.5, would be expected to do so in a continuous manner with increasing anode potential (41).

currents, under steady-state conditions, are manually or automatically recorded. Usually measurements must be made after some standardized periods of time owing to long-time variations in the potential which commonly occur in anodic processes. When such standardization is adopted, the measurements can usually be made very reproducibly.

b. Potentiostatic

Here potential is controlled as the independent variable by means of a rapidly responding feed-back dc-amplifier system, and the values of the current at given controlled potentials, after the steady-state has been established, are recorded.

Both these methods give identical results for electrode reactions where only a simple linear Tafel region is observed. In more complex cases where a Tafel region follows a well-defined transition region, *e.g.*, in the Kolbe and other anodic oxidation reactions, the potentiostatic method is to be preferred as it reveals the detailed structure of the transition region in a way which is not usually accessible under galvanostatic conditions (21, 34, 98, 162). Hence in cases where the transition region is of interest because of the possibility of inhibition or passivation effects, or other complications due to coadsorbed surface species (4, 85, 162, 164), the potentiostatic method is quite essential for full interpretation and study of the electrochemical kinetic behavior of the reaction.

The necessity of control of electrode potential (93, 94) rather than the rate (*i.e.*, current) in organic electrode processes has to be emphasized for a variety of other reasons. Apart from determining the coverage of some electrodes by adsorbed H- or O-containing species derived from the solvent (*i.e.*, in *aqueous* solutions of organic salts), the potential will also be of importance in determining the adsorption of the organic reactant itself. It has not been widely appreciated in work on organic electrochemical reactions that adsorption on the working electrode (determined by the potential of the latter in relation to that of zero charge) is one of the two most important single factors which distinguish electrode processes from other heterogeneous reactions (the second factor being the potential-dependent free energy of activation—Appendix I) (21, 122).

The Tafel slope $dV/d \ln i$ is readily evaluated from experimental logarithmic current–potential curves, obtained either galvanostatically or potentiostatically. A typical log (current)–potential relationship (*i.e.*, a "Tafel" plot) potentiostatically obtained for the Kolbe reaction on platinum in strictly anhydrous 1 M CH_3COOK–CH_3COOH solution prepared in an all-glass apparatus initially under vacuum is shown in Figure 3. In the case of the Kolbe reaction with various reactants and at a variety of electrode metals, the rate-determining step is sufficiently slow ($i_0 < 10^{-13}$ amp cm^{-2}) that direct dc steady-state methods may be used. Fast reaction techniques, such as ac impedance, faradaic rectification, and the analysis of rapid anodic transients are thus unnecessary for kinetic characterization of the *slow step* in the reaction.

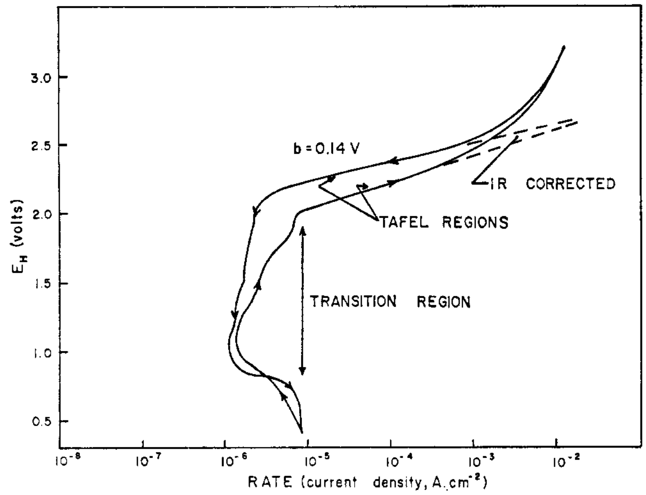


Figure 3.—Steady-state, potentiostatic potential–rate (*i.e.*, current) relationship for the Kolbe reaction on platinum in very anhydrous CH_3COOK (1 M)–CH_3COOH solutions (prepared *in vacuo*) (after Vijh and Conway (164)).

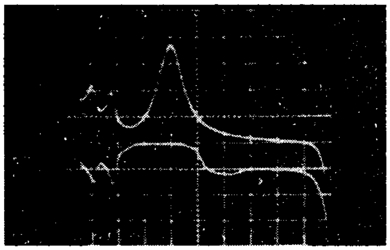
B. NONSTEADY-STATE MEASUREMENTS

A variety of nonsteady-state measurements, which yield information on the nature of adsorbed intermediates or on rate constants, have been used in studies on the Kolbe reaction. The results obtained by the nonsteady-state techniques may be used in a complementary way to those obtained by steady-state log (current)–potential curves for interpreting mechanisms of electrode reactions. Some details will now be considered.

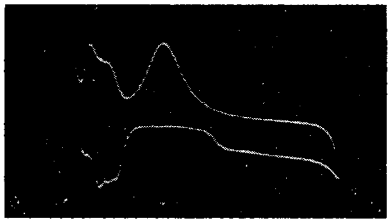
1. *Experimental Techniques*

a. Potentiodynamic Current–Potential Relationships

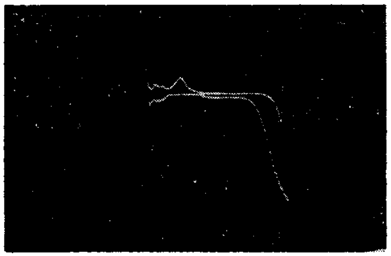
This procedure consists of subjecting the electrode to a repetitive "triangular" or single "ramp" voltage–time sweep at a rate s ($= \pm dV/dt$) usually by feeding a reference signal of this form into a potentiostat and observing, by means of an oscilloscope or an X–Y recorder, the time- and hence potential-dependent relaxation current which passes during the voltage sweep (170). The currents which are measured are usually composite and the charging component must be separated by appropriate methods (21). The transient currents that pass during the sweep are determined in part by a quantity $C_{ads}\, dV/dt$, and it is the quantity dV/dt taking periodically positive and negative constant values which can be varied in this technique from run to run. Here, C_{ads} is the pseudo-capacitance (Appendix II) associated with Faradaic deposition or



(i) Pt in $1M$ H_2SO_4 (0.0–1.8 v)



(ii) Pt in aq ($1M$ CH_3COOK + $1M$ CH_3COOH)(−0.03–1.86 v)



(iii) Pt in aq ($1M$ CH_3COOK + $1M$ CH_3COOH) (−0.06–2.6 v)

Figure 4a.—Some experimentally obtained potentiodynamic profiles for the acetate Kolbe reaction at Pt together with the potentiodynamic current–potential profile for the Pt–H_2SO_4 system: (i) $dV/dt = 3.6$ v sec^{-1}; (ii) $dV/dt = 3.78$ v sec^{-1}; (iii) $dV/dt = 0.8$ v sec^{-1}.

removal of the adsorbed species on the electrode and dV/dt is the rate of change of potential or overpotential of the electrode (21, 24). The transient currents which pass in various potential regions of the sweep may be integrated with respect to time to give approximate estimates of the charge associated with formation or removal of the intermediates, except at potentials where a net over-all (or real Faradaic) reaction begins to predominate or if diffusion effects are significant.

The potentiodynamic method is the electrochemical analog of thermal flash-desorption (20, 21, 40), and the variation of electrode potential plays a role similar to that of programmed change of temperature in the latter technique. The application of single linear potentiodynamic sweeps from prior steady-state conditions is preferable to the use of repetitive sweeps since the single linear sweep then gives information on the presence of, and coverage by, adsorbed species formed in the prior steady state. This procedure, developed by Gilman (83), is then analogous to the galvanostatic pulse method (see section b.ii below).

As examples, three potentiodynamic profiles for the case of the Kolbe reaction on platinum in aqueous acetate–acetic acid solutions are shown in Figure 4a, together with a fourth profile for the case of platinum in 1 M H_2SO_4 solution (for the purpose of comparative interpretation). To facilitate identification of various charging peaks in these profiles, the schematic diagram Figure 4b may be referred to (162, 164). Interpretation of these diagrams is discussed in section VI.A below.

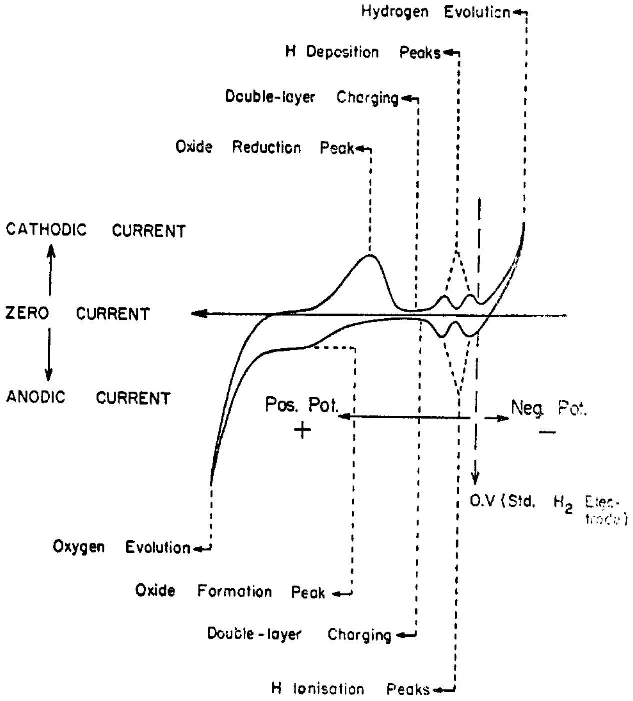


Figure 4b.—Schematic representation of potentiodynamic profile for Pt in aqueous acid solution shown for identification purposes, with regard to Figure 4a and Figure 12.

b. Transient Methods

Here the term "transient methods" is used in the restricted electrochemical sense only and denotes potential–time transients observed on self-discharge or cathodic reduction of electroactive adsorbed species formed at some initial anodic potential.

(*i*) *Self-Discharge Transients.*—Information on the nature of adsorbed intermediates that may be involved in the Kolbe reaction has been obtained by evaluating the adsorption pseudo-capacity (27) from the rate of decay of potential (28) of the working electrode on open circuit following steady-state potentiostatic polarization (25, 34, 162). Thus the rate of decay of potential will be a function of time but will always be determined by the intrinsic electrochemical time constant *RC* of the reaction comprised of an equivalent capacitor and the reaction nonohmic resistance (inversely proportional to the electrochemical rate constant) in parallel (44, 78).

The essential calculations involved and other relevant matters have been discussed elsewhere (17, 21, 27, 28, 44, 78).

(*ii*) *Cathodic Reduction Profiles and Differentiated Curves.*—A fast differential dc charging method (108), in which the potentiostatically maintained initial anodic

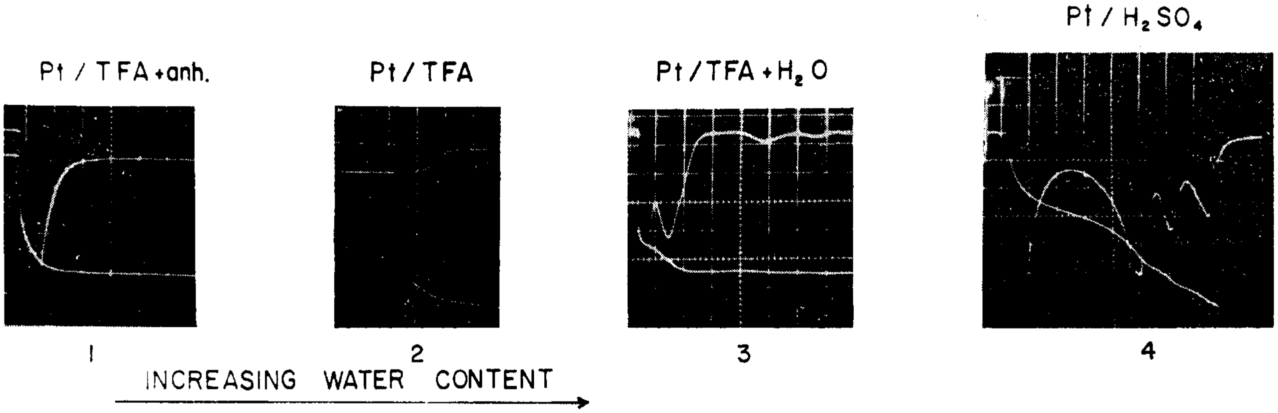


Figure 5.—Constant current transients (5°) (together with the corresponding differentiated profiles) showing cathodic reduction behavior of anodically formed adsorbed intermediates (peak 1), under the indicated conditions; peaks 2 and 3 are for adsorbed hydrogen atom production (33) (charge Q in mcoulombs cm^{-2}): (1) no peak, $Q = 0$; (2) peak 1, $Q = 0.15$; (3) peak 1, 0.71, peaks 2 and 3, 1.87; (4) peak 1, 1.3, peaks 2 and 3, 0.7.

potential may be made to decay by driving it with a relatively high constant current transient, has been used to examine coverage by adsorbed species involved in the Kolbe reaction (Figure 5) (34, 162). In this method, the differential curves [$(dV/dt)_i$ as $f(t)$ and hence V] give directly a quantity which is reciprocally related to the pseudo-capacitance, C, associated with the potential dependence of coverage by adsorbed intermediates (Appendix II). Also accurate values of charge, Q, consumed in the stripping of an electroactive intermediate (formed initially in the steady state of the Kolbe reaction) from the surface of the electrode may be obtained and then related to the coverage of the electrode. This procedure is a significantly modified and more accurate version of charging techniques used previously in the study of a number of anodic reactions including the Kolbe reaction (25, 42).

Details of the historical development of this method and its theoretical and experimental basis have been reviewed elsewhere (21, 78).

(*iii*) *Anodic Charging Curves.*—The reverse of the method described in part ii above has been used by Dickinson and Wynne-Jones (42) who investigated anodic charging transients (Figure 7) in the buildup of the surface oxide layer on Pt in the *approach to* the steady-state of the Kolbe reaction. Method ii gives information on the species already present in a prior steady state; the two approaches are complementary.

c. Pulse Techniques

Pulse techniques, though formally involving transients in a repetitive way, merit a discussion as a separate class of experimental approaches which have been used in the study of the Kolbe reaction. This procedure is the electrochemical analog of the rotating-sector technique used in the study of photochemical gas-phase reactions (15); both pulse techniques and rotating-sector techniques are useful for determining, among other things (70), the orders (71, 173) of reactions in these respective fields of study.

Both current-pulse and potential-pulse techniques have been employed in studies on the Kolbe reaction and involve respectively interrupted current (square-wave signal) or interrupted potential controlled by a potentiostat, the input of which is driven by a function generator prearranged in a square-wave configuration for output voltage. The kinetic interpretation of the results obtained are discussed below (section V.A.2.b).

2. Type of Information Conveyed

(i) Potentiodynamic and transient methods yield the following kinds of information: (a) magnitude of charge Q consumed in the formation (or removal) of intermediates adsorbed on the electrode surface, and hence an estimate of coverage Θ or thickness of an adsorbed layer; (b) magnitude of pseudo-capacitance, C (see Appendix II), associated with the potential dependence of the coverage Θ by adsorbed intermediates, where $C = k\, d\Theta/dV$, k being a constant and V the electrode potential where $k = Q/\Theta$; (c) the potentials at which the various capacity maxima, $C_{\max}$ (*i.e.*, peaks in the differentiated potential decay, cathodic reduction profiles, or potentiodynamic profiles) appear; (d) general shape of capacity–potential profiles which under favorable circumstances can be indicative of the nature of adsorbed intermediates; (e) departures from equilibrium behavior induced in the capacity–potential profiles by applied "perturbations" (*i.e.*, the dependence of the position and shape of the capacity profile on the reduction current in cathodic transient curves and on scan rate in the potentiodynamic profiles) (29) interpreted in some cases as diagnostic of the nature of the surface species involved in the Kolbe reaction (162).

(ii) Pulse techniques are aimed at examining the following matters: (a) the order of the reaction (*cf.* Figure 7, section V.B.2); (b) the values of the rate constants of elementary steps involved consecutively in the over-all reaction, *e.g.*, as applied to the Kolbe reaction (thus, rate constants of steps other than the rds can be evaluated (70)); (c) the possibility of controlling the reaction, mainly by interrupted termination of consecutive chains of reactions, through manipulation of pulse length and height of the pulse signal, *i.e.*, through control of the reactions by relaxation methods (51).

3. *Identification of Adsorbed Intermediates*

For complete elucidation of the mechanism of an electrode process, the kinetic analysis given in section IV.A.1 must be supported, where possible, by knowledge of the identity and nature of any adsorbed intermediates, as well as the final products; however, in electrochemical measurements, the identity of the adsorbed species can usually only be deduced indirectly from the data obtained in various nonsteady-state measurements and from knowledge of the principal products. Here a brief discussion of some of the *general* principles involved in the elucidation of the identity of the adsorbed species is presented.

It must be stressed, however, that identification of adsorbed species by purely electrochemical charging studies can never be chemically certain. Only by using several complementary electrochemical approaches for a given reaction can such methods be of some value. Further elucidation of the identity of adsorbed species may also be obtained in favorable cases by use of^{14} C-labeled reactants (43, 80). However, even this method is not entirely unambiguous since ions specifically adsorbed in the double layer cannot easily be distinguished from chemisorbed species which may arise from discharge of the ions. However, in the case of acetate oxidation, the acetate reactant can be labeled in the C-1 or C-2 positions and any differences in adsorption behavior can then indicate involvement of chemisorbed CH_3 species.

a. Potential of Commencement of the Tafel Region

In a potentiostatic steady-state current–potential curve, the potential at which the Tafel region commences in relation to the behavior of the Tafel line for a known process may enable some preliminary conclusions to be made.

Linear Tafel behavior for the Kolbe reaction on Pt in aqueous acetate solution commences above 2.1 v, suggesting that in the part of transition region from 1.7 v (which is approximately the potential at which the Tafel region for oxygen evolution in acid solutions not containing carboxylate species normally arises at current densities of *ca.* 10^{-6} amp cm^{-2}) to 2.1 v, formation of some adsorbed intermediates (possibly $CH_3COO\cdot$ or $CH\cdot_3$) has perhaps taken place. However, the possibility of oxidation of trace impurities or the occurrence of parallel (side) reactions in this potential range must be recognized. The current densities involved, are, however, too small to allow coulombic analyses to be made.

b. Rest Potential[6]

This can be a qualitative guide (126, 127, 162) to the identity of the species that might be irreversibly adsorbed on the electrode; *e.g.*, if a surface oxide is the only species adsorbed on the electrode, then the rest potential usually approximates to the reversible potential for the oxygen evolution reaction, *i.e.*, 1.23 v or some related mixed potential. If oxide was covering only part of the electrode surface and the remainder of the surface was either bare or partially covered by a species formed in a reaction with a much lower reversible potential, the experimentally observed rest potential could be a mixed potential and could arise roughly between 0.8 and 1.3 v, depending on the proportion of the electrode surface covered by the oxide and the rate constants for the partial processes involved. Here this rest potential, it must be noted, is usually (31) treated in a purely empirical manner.

c. Residual Potential[7]

The residual potential observed on open-circuit emf decay has in practice a significance similar to that of the rest potential.

d. Inhibition Inflection

In certain organic oxidations, a characteristic inhibition inflection or reversal of the direction of the Tafel line is observed in the current–potential relation (4, 85). If a linear Tafel region occurs[8] beyond this passivation inflection, it may indicate either that discharge can occur onto the layer of inhibiting species after that layer has been formed in the steady state to an appreciable extent of coverage, or that a new mechanism arises as the potential is made more anodic. Inflections of this kind are observed for the Kolbe reaction (67).

e. Magnitudes of Q and C

The magnitudes of Q and C calculated from discharge transients or potentiodynamic profiles can, in some cases, be a useful guide to the identity of the adsorbed

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(6) The rest potential may be defined as the potential on the descending log (i)–V curve at which the current just tends to become cathodic. Rest potentials have been found useful in the characterization of adsorbed species in other work, *e.g.*, involving methanol oxidation (126).

(7) The term residual potential refers to the potential attained by the electrode after rapid self-decay of a fraction of its initial polarization potential. The residual potential will thus be the quasi-steady potential that the electrode attains in the absence of depolarizers a few minutes after cessation of polarization. It is usually determined by the presence of irreversibly adsorbed species on the electrode.

(8) We have referred to this as the "post-transition" region in section IV.A.1.

species. Experimentally determined Q values may be compared with theoretically estimated values of Q corresponding, for example, to a monolayer of R·, RCOO·, surface oxide, etc. by assuming a simple model of closed-packed spheres and a plausible roughness factor for the electrode surface, which can often be supported by *in situ* determinations of the electrochemical H accommodation on the same electrode (14). The most probable orientations of these radicals on the electrode surface should also be taken into account.

f. Relation between Solution Composition and Magnitudes of C and Q

Experimental determination of Q and C in very anhydrous solutions and in solutions containing varying amounts of added water may lead to some estimate of contributions in the Q and C values attributable to oxide only, in those solutions (a) where water is present and (b) where coadsorption of oxygenated species is suggested by other evidence.

g. Potentials of Arrests in Cathodic Discharge Profiles

In the C–V profiles, the values of $V_{C_{\max}}$ (*i.e.*, the potentials of the capacity maxima) observed correspond to the potentials of arrests in the respective cathodic discharge profiles. Thus $V_{C_{\max}}$ values can be helpful in the identification of the adsorbed species; *e.g.*, if $V_{C_{\max}}$ lies in the range 0.6–1.0 v, the presence of an oxide would seem to be indicated (4). Also, $V_{C_{\max}}$ often occurs near the potential for half-coverage (27, 28, 85) by the electroactive species involved.

h. Effect of i_{cath} on the C–V Profiles

The effect of i_{cath} (*i.e.*, cathodic current density used in the reduction transient) on $C_{\max}$ (*i.e.*, the capacity maximum) and $V_{C_{\max}}$ may also be of some value in the identification of an adsorbed species. Thus, it can be shown theoretically (29) that for an irreversibly adsorbed electroactive species, an increase in i_{cath} used in the cathodic transient should shift $C_{\max}$ to higher values and $V_{C_{\max}}$ to more cathodic potentials. This effect arises because the capacity measured during a constant current charging process is not the "equilibrium capacity", *i.e.*, it is not the value of capacity that will correspond to the value extrapolated to zero ac frequency if the capacity measurements were made by an ac method, *e.g.*, as in the work of Dolin and Ershler (44). In dc measurements of capacity, a concept of "equivalent frequency" is applicable, as discussed by Conway, Gileadi, and Kozlowska (29), and a theoretical treatment predicts the shifts in $C_{\max}$ and $V_{C_{\max}}$ values with varying i_{cath}. This effect has been to some extent experimentally confirmed by the small amount of data which at present exists in the literature on irreversibly adsorbed electroactive species.

i. Potentials of Peaks in the Potentiodynamic Profiles

The potentials at which peaks appear in the potentiodynamic profiles can be indicative of the identity of the adsorbed species, especially if the profiles have been obtained at slow sweep rates. For example, the peak for the reduction of the adsorbed oxide on Pt appears around 0.6 v (*cf.* Figure 4b) and the two peaks for hydrogen deposition around 0.1–0.3 v on the hydrogen scale for the same solution. The significance of potentials at which the peaks appear in the potentiodynamic profiles is, in principle, similar to that for $V_{C_{\max}}$ in the C–V profiles calculated from the cathodic galvanostatic transients. In the potentiodynamic method, this argument will only apply to peaks that can be justified as being associated with pure charging processes, *i.e.*, when the peak height is proportional to dV/dt and the area under the peak is independent of dV/dt. (In a galvanostatic transient the analogous test is that the transition time τ is inversely proportional to i_{cath}.)

j. Q *vs.* Rate Relations

The principles involved in interpretation of such plots are briefly as follows (31, 162): (a) if *increased Q values* correspond to *decreased rates*, Q would be regarded as being associated with an inhibiting, coadsorbed species; (b) if this Q were associated with an inhibiting species and its observed value was only appreciable when some water was present in the solutions, the inhibiting species would be likely to be adsorbed oxygen containing radicals (OH or O) or a surface oxide; (c) if the magnitude of Q were to increase with increase in the amount of water present in the solution, then it could be assumed that Q was associated with an inhibiting oxide species, discharged from water ($M + H_2O \rightarrow M/OH + H^+ + e$).

k. Q *vs.* V_i Relations

A plot of Q *vs.* V_i, the initial polarization potential, can under favorable cases be another complementary guide to the identity of the adsorbed intermediates (31, 162); *e.g.*, in the case of the Kolbe reaction on gold in CH_3COOK (1 *M*)/glacial CH_3COOH solutions containing traces of water, it is observed that Q increases with increasing V_i, below the commencement of the Tafel region (*i.e.*, 1.9 v), and above this potential Q decreases with increasing V_i (31). If Q were associated with an electroactive Kolbe adsorbed species (and not an inhibiting specie like a surface oxide), it would tend to increase (or remain unchanged) with increasing V_i, well into the Kolbe region. This follows from the consecutive reaction scheme A–E′ in section IV.A.1, where the coverage by intermediate species will usually tend to increase with increasing anode potential.

V. REACTION MECHANISMS. ENERGETIC AND KINETIC ASPECTS

In section A below, thermodynamic considerations will be developed and related to the kinetics of the reaction at the appropriate reversible potentials; in section B, the kinetics of the reaction under conditions of net anodic overpotential will be examined mechanistically.

A. THERMODYNAMIC ASPECTS OF THE KOLBE REACTION

Calculations on the "reversible" potential of the over-all Kolbe reaction and of the individual elementary steps that constitute the over-all Kolbe reaction have been presented in the literature and are examined below.

1. *Latimer's Calculation*

A value of the standard reversible potential for the over-all Kolbe reaction in aqueous acetate solution, given by Latimer, *viz.* 0.12 v, refers to the Kolbe reaction proceeding from CH_3COOH as reactant (110); *i.e.*, referred to the hydrogen electrode half-cell, the over-all process to be considered is

$$2CH_3COOH \longrightarrow C_2H_6 + 2CO_2 + (2H^+ + 2e) \qquad (a)$$

However, experimentally, production of ethane by the above reaction seems unlikely; kinetically, in the solutions usually studied which contain high concentrations of acetate ions, it seems more probable that the reaction proceeds kinetically from ions so that the calculation of the electrode potential is to be made preferably by reference to the reaction

$$2CH_3COO^- + 2H^+ \longrightarrow C_2H_6 + 2CO_2 + H_2 \qquad (b)$$

The value of the standard reversible potential for the Kolbe reaction should, therefore, refer to reaction b.

2. *Calculation of Conway and Vijh (34)*

The standard reversible potential (*i.e.*, on the hydrogen scale) for the over-all Kolbe reaction in aqueous acetate solutions may be calculated as follows (34). As indicated above, the required reaction is step b and may be regarded as consisting of the two elementary reactions

$$\begin{array}{lr} 2CH_3COOH \rightleftharpoons C_2H_6 + 2CO_2 + H_2 & (c) \\ \underline{2CH_3COO^- + 2H^+ \rightleftharpoons 2CH_3COOH} & (d) \\ 2CH_3COO^- + 2H^+ \rightleftharpoons C_2H_6 + 2CO_2 + H_2 & \end{array}$$

where (c) is analogous to (a) above.

From tabulated thermodynamic quantities (135), the following data may be obtained for the standard free energies of formation $\Delta G_f°$ of the species involved (in kcal mole^{-1}): $\Delta G_f°(2CO_2) = -94.25 \times 2 = -188.50$, $\Delta G_f°(C_2H_6) = -7.86$, $\Delta G_f°(2CH_3COOH)_{aq} = -191.02$. Also the p$K_A$ for the reaction

$$CH_3COOH \overset{K_A}{\rightleftharpoons} H^+ + CH_3COO^-$$

is equal to 4.756 and writing

$$\Delta G_A° = -RT \ln K_A$$

$\Delta G_A° = 1.98 \times 298 \times 2.303 \times 4.756 = 6.46$ kcal mole^{-1}.

From the above data, the following $\Delta G°$ values in kcal mole^{-1} may then be obtained: for reaction c, -5.34; for reaction d, -12.92; for reaction b, -18.26. With the well-known relation $\Delta G° = -zFE_H°$, $E_H°$ for the half-cell reaction

$$2e + CO_2 + C_2H_6 \rightleftharpoons 2CH_3COO^-$$

can be calculated on the hydrogen scale as

$$E_H° = -\frac{18.26 \times 4.182 \times 1000}{2 \times 96487} = -0.396 \text{ v}$$

so that the standard reversible potential for the Kolbe reaction in aqueous potassium acetate solutions is -0.396 v (Stockholm convention).

Similarly, using the datum $\Delta G_f°(2CH_3COOH) = -187.6$ kcal mole^{-1}, and a value for p$K_A = 14.61$ (*i.e.*, for the autoprotolysis) estimated from conductivity data (117), the $E°$ value for *nonaqueous* solutions (glacial acetic acid) is found to be -1.05 v.

3. *Eberson's Calculations*

Eberson (46) has reported some interesting calculations of "thermodynamic potentials" for certain of the possible intermediate steps involved in the over-all Kolbe reaction. The relevance of these calculations seems (35), however, to be questionable, since the difference between the reactivity and thermodynamic properties of species when adsorbed and their supposed high reactivity in homogeneous solution was not taken into account. The Kolbe reaction, like all electrode processes, is a heterogeneous reaction, and the discussion of concentration, reactivity, and thermodynamics of an intermediate "free-radical" species is usually relevant only if it refers to species on the surface, *i.e.*, in the adsorbed state (*cf.* Baizer in ref 63). Thus, energies of chemisorption, *e.g.*, of RCOO· or R·, must be taken into account (see Table I) in any thermodynamic calculations of potentials for partial reactions (although not, of course, for the whole over-all reaction). Only when radical ions are produced, *e.g.*, in the electrooxidation of anthracene, does it seem that radicals can exist for some time in the solution phase. In such cases, their desorption or direct formation in solution is favored by solvation effects. It is unlikely that the product hydrocarbon, R_2, is produced homogeneously from radicals R· after an initial ion-discharge step, except possibly if R· is large and the solvent has strong physical affinity for R·, *i.e.*, for nonaqueous media. Similar comments apply to the calculations of Sasaki, *et al.*

(138), who realized, however, the possible involvement of adsorbed R· radicals but did not apparently take it into account in their thermochemical calculations. In the latter work, the probability of various reaction paths and intermediates was also based only on *enthalpy* data. It is clear that, in general, the free energies are really required and the conclusions from this work may be in error on this account as well as on account of the neglect of chemisorption effects. Thus, in reactions proceeding at surfaces, the entropy effects can be particularly significant and cannot (when multiplied by T) usually be neglected in comparison with the enthalpy terms. Similarly, when the adsorbed species, *e.g.*, RCOO·, arises from an ion ($RCOO^-$), the entropy change might be anticipated to be quite appreciable due to desolvation effects. In many other reactions, *e.g.*, evolution of H_2, O_2, N_2, oxidation of formate to CO_2, or oxidation of hydrocarbons, adsorbed radical species are indicated by direct and indirect electrochemical procedures, so it is unlikely that the Kolbe reaction proceeds by a fundamentally different mechanism involving production of R· or RCOO· in solution and the homogeneous decomposition of discharged RCOO· and subsequent recombination of 2R· (32) to give the Kolbe product R_2.

Finally, it is to be noted that predictions of reaction products by purely thermodynamic calculations for a reaction as irreversible as the Kolbe reaction ($i_0 < 10^{-13}$ amp cm^{-2} at Pt, 25°) is unrealistic. The type of products formed in various possible (parallel) pathways will depend on (a) the relative values of the rate constants for various steps and (b) the potential dependence of the rates of such steps (81). Steps which may appear thermodynamically feasible may be kinetically unrealizable. Normally, the only thing that can be kinetically concluded from the thermochemical data is that (a) for endothermic processes, the activation energy will be at least as large as the endothermicity; and (b) the over-all Kolbe reaction will not proceed under any circumstances or conditions at potentials cathodic to the over-all reversible potentials discussed and derived above.

4. Comparison of Reversible Potentials for the Kolbe Reaction in Aqueous and Nonaqueous Media (34)

a. Aqueous Case

Here we require the $\Delta G°$ for the reaction

$$2CH_3COO^- \rightleftharpoons C_2H_6 + 2CO_2 + 2e$$

on the hydrogen scale. Combining this half-cell reaction with the reaction

$$2e + 2H^+ \rightleftharpoons H_2$$

the required $\Delta G°$ for the $E°$ on the hydrogen scale is obtained, as considered above, *i.e.*, $E° = -0.396$ v (see section V.A.2).

The actual E value for any condition is

$$E = E° - \frac{RT}{2F} \ln \frac{(a_{H^+})^2(a_{OAc^-})^2}{P_{C_2H_6}P^2_{CO_2}P_{H_2}} = E° - \frac{RT}{F} \ln (a_{H^+}a_{OAc^-})$$

at a standard pressure of the gases. Now in aqueous solution of the acid

$$a_{H^+}a_{OAc^-} = K_{A(aq)}$$

Hence

$$E = E° - \frac{RT}{F} \ln K_{A(aq)}$$

for standard gas pressure.

b. Nonaqueous Case

It has been assumed above that the standard free energy of formation of CH_3COOH in aqueous and pure acetic acid is approximately the same (the actual difference, according to Latimer, is 1.71 kcal). Hence the only difference in the calculation for the nonaqueous case is that the K_A is different and the actual reversible hydrogen potential will be different. Therefore the actual reversible potential for the Kolbe reaction will be

$$E_{nonaq} = E°_{nonaq} - \frac{RT}{F} \ln K_{A(nonaq)}$$

again for standard gas pressures. The $E°_{nonaq}$ will differ, however, from that in aqueous media because the K_A is involved in the $\Delta G_A°$ in the ionization reaction (d) considered above.

However, these K_A terms involved in the calculation of E for nonaqueous and aqueous medium cancel out, so that the actual reversible potentials E against the $H_2|Pt$ electrode in the same solution are *identical.* Differences in the actual measured rates of the Kolbe reaction in aqueous and nonaqueous medium (see below) can therefore, from an electrochemical point of view, be properly and directly compared at the same *numerical value* of measured potential on the hydrogen scales for the respective two types of solution (*i.e.*, with respect to $H_2|Pt$ electrodes in the same solutions as the working electrodes at which the Kolbe reaction is under study).

5. Kinetic Behavior at the Reversible Potential

It is important to emphasize that $E_H°$ for the overall reaction

$$2CH_3COO^- + 2H^+ \longrightarrow C_2H_6 + 2CO_2 + H_2$$

is the same at any metals which might be used as anodes. However, the values of the exchange current density, i_0, may differ substantially at various types of anode for normal kinetic reasons (*cf.* 5, 6, 21). For a series of metals, this i_0 value may be different because it is indirectly related to the work function ϕ, for a

Table III

Reversible Potentials (Stockholm Convention) (34), Exchange Currents (35), and Tafel Slopes (34, 164) for the Kolbe Reaction with Acetate

	E_{H^0}, v	Log i_0, amp cm^{-2}	b, v
Aqueous 1 N CH_3COOK[a] in 1 N CH_3COOH, 25° (lower region of Tafel line, above transition region)	−0.396	−18.4	0.26
Aqueous 1 N CH_3COOK in 1 N CH_3COOK, 25° (upper region of Tafel line)	−0.396	−26.2	0.165
Nonaqueous CH_3COOH anhydrous with 1 N CH_3COOK	−1.05	−25.9	0.14

[a] The value calculated by Latimer (110) for the CH_3COOH case appears to be quoted with the wrong sign.

given metal. The dependence of free energy of adsorption of a particular adsorbed intermediate on the work function ϕ for the adsorbent metal gives rise to different i_0 values for a series of different metals [*cf.* the case for hydrogen evolution and adsorption (24)]. Thus, the heat of adsorption (23, 24) and hence coverage effects (123) determine in part the rates of electrode processes at the reversible potential. The same considerations also apply to the rates of electrode processes at potentials further removed from the reversible potential. This concept is one of some importance in considering the different rates of the Kolbe reaction (or any other electrode reaction for that matter) at a given overpotential for a series of metal electrodes studied under otherwise identical conditions and constitutes the foundations of electrocatalysis (8, 10). In studies of organic electrode processes, particularly the Kolbe reaction, the relevance of these rather fundamental factors in determining the influence of anode material on the rate of the reaction has usually not been considered.

The $E_H°$ value for reaction a in nonaqueous medium (pure CH_3COOH as solvent) will differ from that calculated above through the difference of ionization constant of acetic acid in water and in itself (through autoprotolysis determined by the autoprotolysis constant) as solvent; however, the value of the actual reversible potential against the hydrogen electrode in the *same* solution, where a_{H^+} is determined by the ionization equilibrium, is identical with the value in aqueous solution, as shown above. Data are tabulated below. These potentials then enable the exchange currents i_0 to be evaluated for various conditions as shown in Table III.

B. SOME TYPICAL MECHANISTIC PROPOSALS

1. *Mechanisms from Tafel Slope and Transient Studies*

Dickinson and Wynne-Jones (42) were the first authors to apply methods involving determination of Tafel slopes, observation of charging transients (Figure 6), and related effects to the study of the Kolbe reaction.

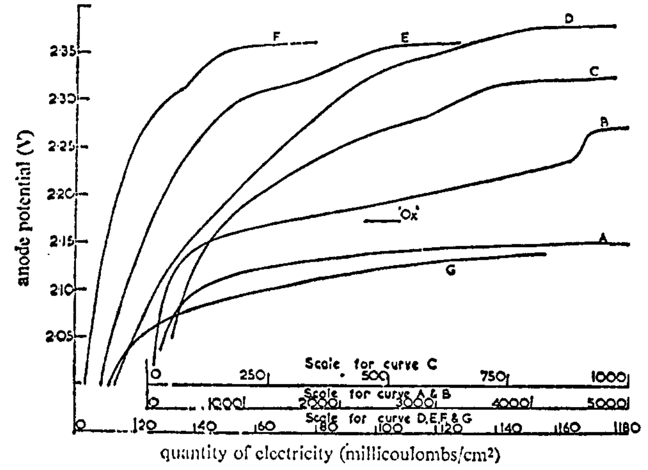

Figure 6a.—Anodic charging curves with platinum electrodes. "Pretreated" electrodes in acetate solutions at current densities (ma cm^{-2}) of 1.75 (A), 2.1 (B), 5 (C), and 25 (D). "Reduced" electrode (E) and cathodically polarized electrode (F) in acetate solution at 25 ma cm^{-2}. Citrate solution at 25 ma cm^{-2} (G) (after Dickinson and Wynne-Jones (42)).

At the same time, Conway and Dzieciuch (26) discussed the origin of the transition region in the current–potential curves and related it to arrests observed in galvanostatic cathodic discharge curves taken from prior steady states at Pt and Au in trifluoroacetate solutions.

In the work of Dickinson and Wynne-Jones, electrolysis of aqueous acetate solutions was carried out and the mechanism of the Kolbe reaction was examined at Pt, Ir, and Au anodes in these solutions. They observed (i) high Tafel slopes (>120 mv) on platinum; (ii) the presence of adsorbed intermediates on the electrode as indicated by the discontinuities in the charging curves (Figure 6a) for electrodes prepared in various ways; (iii) an absence of any detectable Kolbe reaction on gold (*cf.* ref 169) in aqueous acetate solutions (Table V); and (iv) a critical current for the Kolbe reaction at 2.1–2.25 v (*cf.* ref 26). All these observations have been confirmed by other workers (see below).

The galvanostatic charging curves obtained (Figure 6a) by Dickinson and Wynne-Jones were more or less similar to those found for Pt in aqueous oxyanion acids, but after ethane evolution the arrest in the cathodic curves was some 50–100 mv lower than in the case of an electrode at which only O_2 had been generated (*cf* Figure 13). Also the charge required to restore ethane evolution after a cathodic treatment (curve A, Figure 6b) was usually much larger than that (curve B, Figure 6b) required to re-form the surface oxide film, indicating that the former process was inefficient (coevolution of O_2 with the C_2H_6 was suggested) and some further changes in the oxide film (*e.g.*, coadsorption of CH_3·

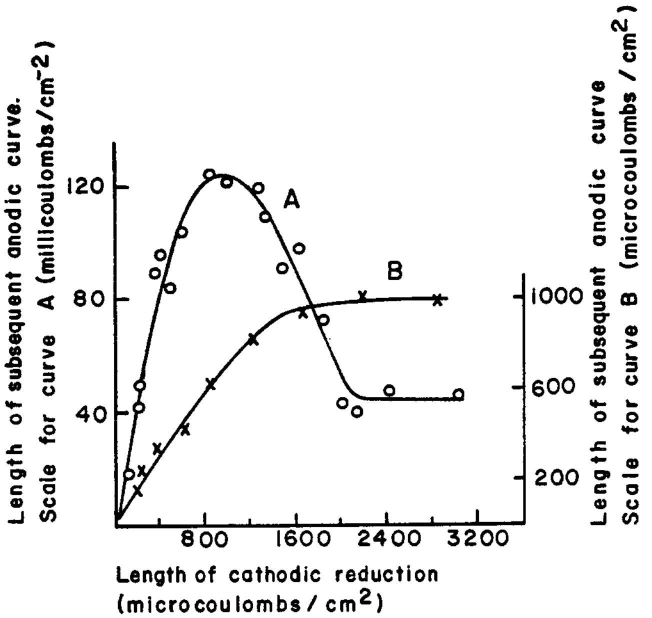

Figure 6b.—Effect of length of cathodic pretreatment of a Pt electrode on the subsequent anodic behavior with regard to ethane evolution and surface oxide formation in the acetate Kolbe reaction: (A) quantities of electricity Q_{Et} required to restore ethane evolution; (B) quantities of electricity required to re-form surface oxide layer, Q_{ox} (after Dickenson and Wynne-Jones (42)).

or $CH_3COO\cdot$; *cf.* ref 164) other than its formation were therefore required for efficient coupling in the aqueous system. In the cathodic (dis)charging curves observed at Pt when the Kolbe reaction was proceeding, no new arrests were observed in comparison with the situation for O_2 evolution (*e.g.*, from aqueous H_2SO_4 alone). This result has been confirmed by the potentiodynamic method (164) and for trifluoroacetate electrolysis (Figure 13).

In their treatment of the above results, Dickinson and Wynne-Jones suggested a mechanism which requires some discussion in relation to the electrochemical kinetic analysis of the reaction which can be made in terms of consecutive reactions. A brief examination of their conclusions is therefore given below.

According to Dickinson and Wynne-Jones, at low current densities, OH radicals are discharged at, and subsequently removed from, the electrode (Pt or Ir) in preference to acetate radicals, a situation which results in the predominant evolution of O_2 with little participation of the Kolbe reaction. This view seems reasonable and is supported by later work. Above a critical current density, discharge (and subsequent decomposition and desorption) of acetate radicals is favored over discharge of OH radicals, a situation which results reasonably in the occurrence of the Kolbe reaction with inhibition of O_2 evolution. It is postulated that at *higher* current densities, at which the Kolbe reaction proceeds more efficiently, acetate ions are discharged on an electrode already fully covered in the steady state by acetate radicals. When the second acetate radical is produced at a site already occupied by a previously discharged acetate radical, "the presence of two acetate radicals on one site causes instability, and degradation occurs giving CO_2 and C_2H_6 *via* the intermediate formation of CH_3 radicals." Desorption of the methyl radicals then occurs to give the Kolbe coupling product. On Au and Ni, it was found that the Kolbe reaction did not occur even at the highest current densities used ($\sim$30 ma/cm^{-2}); only oxygen evolution took place.

The experimental Tafel slopes reported by these authors are as follows, for electrodes at which the Kolbe reaction proceeds.

Metal	Tafel slope, mv		Transition region
	Lower region	Upper region	
Pt	170	130	Well-defined
Ir	Not well-defined	120	Well-defined

These authors did not put forward a scheme of consecutive elementary processes that might be involved in the over-all Kolbe reaction involving transfer of two electrons. Although not stated explicitly, it is implied in the discussion of Dickinson and Wynne-Jones that the rate-determining process is the chemical desorption of two methyl radicals from the "same" site. Since it is supposed that the electrode is more or less fully covered with acetate radicals, it follows that the initial discharge step ($CH_3COO^- \rightarrow CH_3COO\cdot + e$) and the subsequent heterogeneous step producing methyl radicals on the electrode surface ($CH_3COO\cdot \rightarrow CH_3\cdot + CO_2$) must have rate constants greater than that for the final methyl radical recombination step which results in the formation of the Kolbe product C_2H_6 by desorption and recombination of two methyl radicals ($CH_3\cdot + CH_3\cdot \rightarrow C_2H_6$). In the reaction sequence proposed by Dickinson and Wynne-Jones, a detailed mechanism of production of C_2H_6 from discharged $CH_3COO\cdot$ was not proposed explicitly. It is stated that the C_2H_6 arises from discharge of two acetate species at the same site through the intermediate formation of $CH_3\cdot$ radicals. However, kinetically it seems necessary and preferable to separate this process into two steps involving the decomposition of the $CH_3COO\cdot/M$ ($\rightarrow M/CH_3\cdot + CO_2$) and the subsequent recombination of $CH_3\cdot$ radicals, *viz.*

$$2CH_3\cdot/M \longrightarrow 2M + C_2H_6$$

Then if the rate constant for the desorption step were greater than that for either of the first two steps suggested above, the electrode would not be fully covered with methyl radicals. Thus, in general, in terms of *their* mechanism, appreciable coverage will tend to arise if the rate constant for the "desorption" process is less than that for the discharge step at all potentials, *i.e.*, when the former step is rate determining. A deduction of the Tafel slope for the reaction under these conditions (*i.e.*, fully covered electrode with desorption as the rate-determining step) would predict a trend toward a limiting current (infinite Tafel slope) and not the finite Tafel slopes observed by Dickinson and Wynne-Jones. Hence, the conclusions of these authors do not seem to be consistent with the electrochemical kinetic analysis of the problem that would follow in terms of consecutive reactions.

The origin of the difficulty which arises here is that in the work of Dickinson and Wynne-Jones, the over-all process was not discussed in terms of all the kinetically distinguishable (consecutive) elementary processes which seem likely to be involved, nor were the consequences quantitatively evaluated in terms of values of the theoretically predictable Tafel slope parameter *b*.

Conway and Dzieciuch (25) applied these approaches (*i.e.*, the interpretation of Tafel slopes in relation to the results of transient studies) to the study of the Kolbe reaction in anhydrous and aqueous trifluoroacetate solutions, a system which was chosen to minimize side oxidation reactions and hydrogen atom abstraction which can occur with more facility when $R = CH_3$, for example. These authors extended modern quantitative ideas regarding kinetics of consecutive reactions (6, 7) to the study of the Kolbe reaction. They made an analysis, both theoretical and experimental, of the various possible elementary events involved consecutively in the over-all Kolbe reaction and deduced associated Tafel slopes for various conditions of adsorption of the intermediates (see section IV.B.A.1). In this work, the relation between the Tafel slopes and the electrochemical behavior of the adsorbed intermediates was stressed. Also the Tafel slopes were discussed in terms of the behavior of a surface on which "induced heterogeneity" or intrinsic heterogeneity could arise.

In general, high Tafel slopes (>120 mv) were observed and were related to the general features of the kinetics and the behavior of the adsorbed species associated with the reaction, by considering a dipole barrier-layer model (see section IV.A.1) (Figure 2). It was suggested that a fraction $1 - \alpha$ of the total metal–solution potential drop ΔV operated across a dipole barrier-layer of "Kolbe" adsorbed species (*i.e.*, $CF_3COO\cdot$ or $CF_3\cdot$) and was hence unavailable for assisting the interfacial charge-transfer process. The rate of the latter process would then be an exponential function of a fraction β of αV, where β has the usual significance of a symmetry factor. The over-all exponential dependence of rate on V would then depend on the value of the apparent symmetry factor $\alpha\beta$, where $\alpha\beta$ will usually be appreciably smaller than 0.5 and hence give rise to anomalously high Tafel slopes, such as are observed. On the basis of this model, an electrochemical desorption step, *i.e.*

$$CF_3\cdot\ (M) + CF_3COO^- \longrightarrow C_2F_6 + CO_2 + e$$

was concluded to be a probable rate-determining stage, with appreciable coverage by the polar CF_3 or $CF_3\cdot COO\cdot$ radicals providing the dipole barrier film (163).

However, the following comments may be made about the work of these authors. (i) Possible proposals alternative to the dipole barrier-layer model for interpretation of anomalously high Tafel slopes (>120 mv) were not, at that time, examined (*e.g.*, *cf.* ref 164). (ii) The electrochemical measurements reported by these workers were carried out only under galvanostatic conditions. The galvanostatic measurements, as it may be recalled (see section IV.A.2), are not as satisfactory as controlled-potential techniques for studies on organic electrode reactions. However, in later work, potentiostatic procedures were employed (162–164). (iii) The role of surface oxides that may be coadsorbed with Kolbe adsorbed species in the aqueous reaction media was not examined in any systematic way; this problem was also examined, however, in later papers (33, 34) by the present authors.

Fukumoto, Tamura, Hayashi, and Ishida (75) carried out studies on the Kolbe reaction involving steady-state anodic polarization measurements and the determination of charging curves. Tafel slopes >120 mv were again observed in the Kolbe region for platinum in aqueous acetate solutions. A mixed discharge of OH^- and OAc^- ions was concluded and an adsorbed layer of acetate radicals was indicated (*cf.* ref 25). These observations support the previous work of Dickinson and Wynne-Jones in this system, as also did the observation of the absence of any Kolbe reaction on gold in aqueous acetate solutions (Tafel slope $b = 0.055$).

Involvement of chemisorbed $CH_3COO\cdot$ in the Kolbe reaction films of the type suggested by Conway and Dzieciuch (25) has also been concluded on the basis of capacitance measurements on platinum in aqueous acetate solutions (86).

Recently (31, 34, 162–164) the Kolbe reaction has been examined by studying the kinetic behavior under potentiostatic and potentiodynamic conditions (see sections IV.A.2 and IV.B.1.i). The experiments were so designed that the role of coadsorbed surface oxides (arising from the presence of water) in the Kolbe reaction could be determined in a more unambiguous way (31). Differences in kinetic behavior in aqueous and nonaqueous media were investigated. The following are the salient features of the results obtained in these investigations.

(i) In general, high Tafel slopes (see section IV.A.1) were observed both at platinum and gold in strictly anhydrous, "nominally" anhydrous, and aqueous $CF_3COOK–CF_3COOH$ solutions. These slopes were interpreted on the basis of the dipole barrier-layer model referred to above (Figure 2) (25); however, alternative proposals that may be used to interpret the

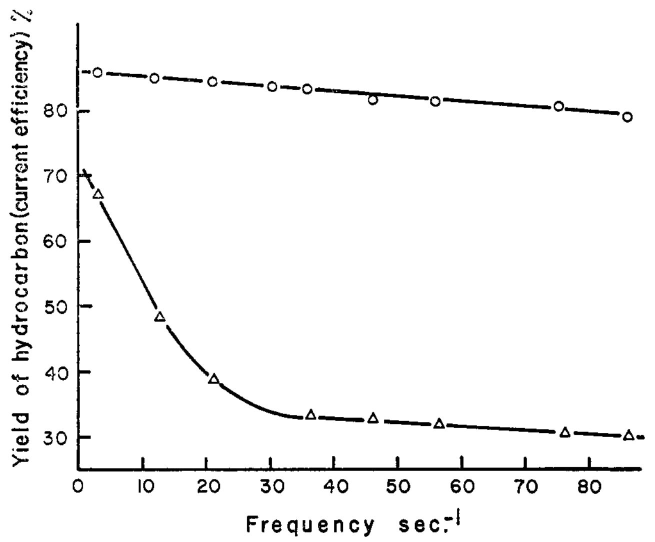

Figure 7.—Effect of frequency on ethane and ethylene formation during square-wave electrolysis of aqueous acetate and propionate (current density, 0.45 A cm^{-2}, 25°: ○, ethane from 5.0 *M* HOAc, 0.5 *M* KOAc in H_2O; △, ethylene from 5.0 *M* HO_2C-Et, 0.5 *M* KO_2CEt in H_2O) (after Wilson and Lippincott, 173).

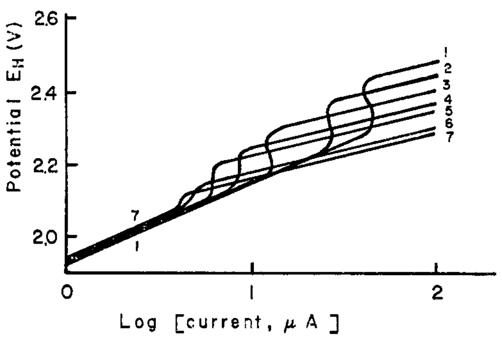

Figure 8a.—Potentiostatic current-potential curves for the acetate Kolbe reaction at 25° showing characteristic inhibition effects at high potentials, dependent on the sodium acetate activity (after Fioshin and Vasil'ev (67)): curves 1 to 7, 0.1 to 4.0 *N*, 25°.

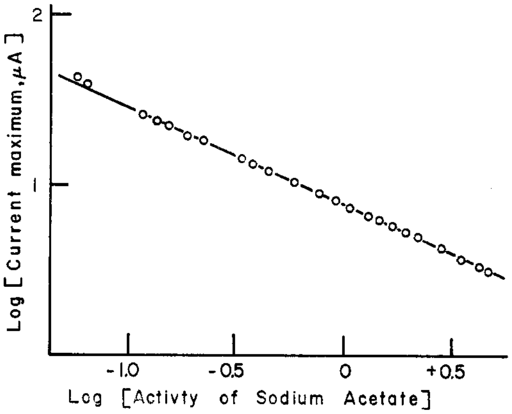

Figure 8b.—Dependence of the log of the current maxima in Figure 8a on the log of the activity of sodium acetate (67).

observed high Tafel slopes under certain conditions were also critically examined (164).

(ii) Identities of adsorbed intermediates were indicated by developing certain correlations (see section IV.B.3) (31, 162) mentioned previously.

(iii) It was concluded that surface oxides that arise from water in the aqueous media are coadsorbed with the Kolbe adsorbed species on the electrode surface and that these coadsorbed oxides cause partial or complete inhibition of the Kolbe reaction (see section VI.A) (33), depending on the anode metal.

(iv) Mechanistic proposals for the Kolbe reaction on platinum and gold in several types of solution are summarized in Table V (162). These proposals are interpreted in terms of the general principles which have been developed in sections IV.A.1 and IV.B.3 in the foregoing discussion.

2. *Mechanisms from Pulse Studies*

Wilson and Lippincott (173) reported, on the basis of constant current pulse studies ("square-wave electrolysis"), that the kinetics of the Kolbe reaction were first order in acetoxy radicals both in nonaqueous and aqueous acetate media (Figure 7). This conclusion seems to be supported in a complementary way by the work of Fioshin and Vasil'ev (67) who observed that under potentiostatic conditions, current maxima arose (*cf.* Figure 13) and these maximum currents (Figure 8a) varied linearly with the activity of the acetate and passed through the origin; *i.e.*, discharge of OAc^- ions is a *first-order* process (Figure 8b). The inflections observed in the current-potential relations are characteristic of inhibition effects (4, 85). This seems to support either a simple ion-discharge mechanism or the electrochemical desorption mechanism for the Kolbe reaction on platinum in aqueous acetate solutions, suggested by Vijh and Conway (Table IV) (164), *i.e.*, $CH_3COO\cdot$ (M) + $CH_3COO^- \rightarrow C_2H_6 + 2CO_2 + e$ as the rds in the over-all reaction where both ions *and* radicals are involved, the latter being present at a coverage approaching unity if the desorption mechanism is to be first order in OAc^- (see below).

The moisture content in the "nonaqueous" solutions used by Wilson and Lippincott (or in those of Conway and Dzieciuch) was probably not nearly as low as in more recent experiments of Conway and Vijh, specially conducted *in vacuo;* hence perhaps the discrepancy for the nonaqueous case (see Table V), in that Conway and Vijh conclude the reaction to be zero order in acetate *radicals* (but first order in acetate ions, of course), whereas Wilson and Lippincott report the reaction to be first order in acetate radicals (*cf.* ref 67), may arise from the presence of traces of water.

It is to be noted (30, 161) that several mechanisms or conditions can correspond to first-order kinetics. (i) Direct discharge of acetate ions at high concentrations or in the presence of excess indifferent electrolyte

TABLE IV

SUMMARY OF SOME MECHANISTIC CONCLUSIONS[a] FOR THE CH_3COOK AND CF_3COOK KOLBE REACTIONS

Electrode (solution)	Water content	b, v	Probable identity of adsorbed species	Possible rate-determining step[a] (rds)
Pt (1 *M* CF_3COOK–CF_3COOH)	(i) None	0.25	A barrier-layer film of $CF_3\cdot$	$CF_3\cdot\ (M) + CF_3COO^- \rightarrow C_2F_6 + CO_2 + e$
	(ii) Traces	0.22	A barrier-layer film of $CF_3\cdot$ with $CF_3COO\cdot$ + some coadsorbed surface oxide	$CF_3\cdot\ (M) + CF_3COO^- \rightarrow C_2F_6 + CO_2 + e$
	(iii) Excess	0.25	A barrier-layer film of $CF_3\cdot$ with $CF_3COO\cdot$ + some coadsorbed surface oxide	$CF_3\cdot\ (M) + CF_3COO^- \rightarrow C_2F_6 + CO_2 + e$ (with some O_2)
Au (1 *M* CF_3COOK–CF_3COOH)	(i) None	0.16	A barrier-layer film of $CF_3COO\cdot$	$CF_3COO\cdot\ (M) + CF_3COO^- \rightarrow C_2F_6 + 2CO_2 + e$
	(ii) Traces	0.175	A barrier-layer film of $CF_3COO\cdot$ + some co-adsorbed surface oxide	$CF_3COO\cdot\ (M) + CF_3COO^- \rightarrow C_2F_6 + 2CO_2 + e$
	(iii) Excess	0.17	A barrier-layer film of $CF_3COO\cdot$ + some co-adsorbed oxide	$CF_3COO\cdot\ (M) + CF_3COO^- \rightarrow C_2F_6 + 2CO_2 + e$
Pt (1 *M* CH_3COOK–CH_3COOH)	(i) None	0.14	None	$CH_3COO^- \rightarrow CH_3COO\cdot\ (M) + e$
	(ii) Excess	0.26 0.165	A barrier-layer film of $CH_3COO\cdot$ + some co-adsorbed oxide	$CH_3COO\cdot\ (M) + CH_3COO^- \rightarrow C_2H_6 + 2CO_2 + e$
Au (1 *M* CH_3COOK–CH_3COOH)	(i) Traces	0.11	A barrier-layer film of $CH_3COO\cdot$ + some coadsorbed oxide	$CH_3COO\cdot\ (M) + CH_3COO^- \rightarrow C_2H_6 + 2CO_2 + e$
	(ii) Excess	0.09	Surface oxide (thicker than at Pt)	Only O_2 evolution

[a] At the moment, some of these mechanisms are still tentative but are the ones which are most consistent with the presently existing experimental evidence.

TABLE V

YIELDS OF C_2H_6 AND O_2 IN ACETATE ELECTROLYSIS AT VARIOUS METALS[a]

Electrode material	Electrolyte concn, *M*	Current density, ma cm^{-2}	Anode potential, v	% of[b]			Current efficiency of ethane formation
				CO_2	O_2	C_2H_6	
Pt	1.0	1.5	2.10	19.1	73.7	0	0
		2.2	2.23	35.7	37.1	16.7	6.1
		14.8	2.34	55.2	2.8	34.6	60.8
		138.5	2.48	61.0	2.5	33.1	79.5
Ir	1.0	0.25	1.72	14.7	49.3	0	0
		0.5	2.01	31.9	42.8	17.4	7.7
		7.0	2.15	56.3	2.7	39.4	70.7
		84.2	2.30	54.6	2.2	40.6	85.0
Pt	0.1	17.0	2.16	4.6	84.3	0	0
		19.75	2.39	15.2	65.8	13.9	8.2
Au	1.0	30.0	1.91	5.4	90.2	0	0
Ni	1.0	30.0	1.77	3.2	95.1	0	0

[a] Based on data of Dickinson and Wynne-Jones (42). [b] Authors' figures for percentages; presumably other residual gases were present.

(when double-layer ψ-potential effects are eliminated) will give rise to first-order kinetics at constant electrode potential. (ii) Decarboxylation of adsorbed $RCOO\cdot$ radicals will be a first-order heterogeneous process so long as the coverage by $RCOO\cdot$ species is proportional to the concentration of $RCOO^-$ ions in solution. This can arise under low coverage conditions strictly only when a Langmuir-type isotherm may limitingly apply (it may arise in practice for limiting conditions when other isotherms apply). (iii) Electrochemical desorption pathways may be pseudo-first order, *e.g.*

$$RCOO\cdot\ (M) + RCOO^- \longrightarrow R_2 + 2CO_2 + e$$
$$R\cdot\ (M) + RCOO^- \longrightarrow R_2 + CO_2 + e$$

if fractional coverage by $RCOO\cdot$ or R approaches unity or if for any other reason coverages $\Theta_{R\cdot}$ or $\Theta_{RCOO\cdot}$ were independent of carboxylate ion concentration. The first of the above desorption mechanisms was suggested for the acetate Kolbe reaction by the present authors (Table V) (162, 164) as the rate-determining step in the over-all reaction.

Since the pulsed electrolysis method offers the possibility of obtaining information of a different kind from that derived from steady-state measurements, the theoretical basis of "square-wave electrolysis" can, with advantage, be considered (20, 70, 173).

This method can be used to distinguish between a first-order and a second-order rate-determining stage (rds) in a sequence of processes constituting the over-all reaction and to obtain rate constants for individual steps. Experimentally, the dependence of product yield on pulse length (*i.e.*, time at a given potential) is examined, and this information is related to the order of the rds as follows. Here it is tacitly assumed (a) that the pulse height (*i.e.*, in terms of anode potential) is adequate to sustain the Kolbe reaction; *i.e.*, the anode potential reached during the pulse is above *ca.* 2.2 v (*vs.* the hydrogen electrode in the same solution); and (b) that the pulse frequency is not so high as to inhibit the Kolbe reaction in favor of complete oxidation of CH_3COO^- to CO_2 and H^+ (70); in fact, the relative yields of Kolbe dimer and Hofer–Moest oxidation products are found to be a function of pulse frequency.

Suppose that in the Kolbe reaction X is an intermediate radical, *e.g.*, RCOO·, and that X can form the products P by a series of consecutive events, one of which is the rds and is either first or second order.

If the rds is assumed to be first order, the time dependence of [X] and [P] is

$$d[X]/dt = I = k_1[X] \qquad \text{(Eq 1)}$$

and

$$d[P]/dt = k_1[X] \qquad \text{(Eq 2)}$$

where concentrations refer to mole $l.^{-1}$ or cm^{-2} of surface, I is a measure of total equivalents of electricity passed per sec cm^{-2}, and k_1 is the specific rate constant for the (assumed) first-order process.

Integration of Eq 1, substitution in Eq 2, and subsequent integration of Eq 2 gives, to a first-order approximation,

$$[P] = It - \frac{I}{k_1}(1 - e^{-k_1t}) \qquad \text{(Eq 3)}$$

Similarly, if the rds is now assumed to be second order, then

$$[P] = It/4(1 - t\sqrt{Ik_2}) - (\sqrt{I/k_2}) \ln (2) \qquad \text{(Eq 4)}$$

The quantity It represents coulombs passed in one pulse cycle, and $[P]/It$ is hence a current efficiency factor E for product yield expressed by

$$E_1 = 1 - (f/k_1)(1 - e^{k_1/f}) \qquad \text{(Eq 5)}$$

and

$$E_2 = (1/4f)(f - \sqrt{Ik_2}) - f \ln 2/\sqrt{Ik_2} \qquad \text{(Eq 6)}$$

where f is a measure of frequency ($f = 1/t$). These equations indicate that if the rds is first order, the current efficiency will be linear in frequency and will tend to decrease only slightly at higher frequencies. However, if the radicals formed disappear by a reaction sequence involving a second-order rds, the relationship is more complex but will give a rapidly falling current efficiency at high values of frequency. Some experimental results obtained by the "square-wave electrolysis" procedure are shown in Figure 7.

In another brief investigation of the Kolbe reaction by a repetitive potential–pulse technique (71), it was concluded that the ethane formation proceeds by a *second*-order reaction between acetate radicals. This would imply, in terms of Tafel slopes (in steady-state experiments, a mechanism involving recombination between acetoxy radicals as the rate-determining stage (see section IV.1.A and Table II). The predicted Tafel slope in that case would be 30 mv (at low coverages) or a limiting current (at high coverage); this mechanism, therefore, is one of the few that can be unambiguously refuted by the Tafel slope evidence provided from the work of several investigators (see section V.B.i above) who have consistently observed Tafel slopes which are greater than 120 mv and hence well beyond[9] the 30-mv limiting value.

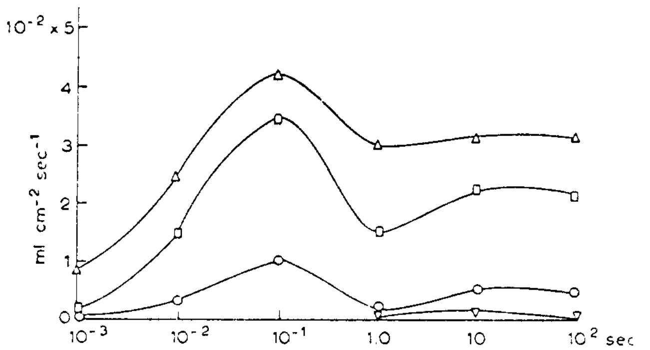

Figure 9.—The integral yield of ethane as a function of prior oxidation time for an electrolyte 1 *M* NaOAc + 1 *M* HOAc: oxidation potentials (v) of 2.2 (▽), +2.35 (○), +2.55 (□), +2.7 (△) (long polarization times) (after Fleischmann, Mansfield, and Wynne-Jones (70)).

A repetitive potentiostatic pulse technique has also been applied (70) in a more sophisticated manner to the study of the Kolbe reaction on platinum in aqueous acetate solutions; in this investigation, an attempt was made to develop the essential nonsteady-state theory for the production of Kolbe and other products under the conditions that obtain in the above technique. On the basis of investigations reported, it was concluded that initial discharge of the acetate ions is the rate-determining step. These investigations consisted of (i) a study of current–time transients that follow an applied potential pulse; (ii) an examination of the form of variation of the yield of ethane with time and its dependence on potential (Figure 9). Among the experimental observations of these authors, the following are to be specially noted: (i) that at pulse lengths shorter than 10^{-3} sec, *complete* oxidation of the acetate ions takes place and involves the suggested sequence

$$CH_3COO^- \longrightarrow CH_3COO\cdot\ (M) + e$$
$$CH_3COO\cdot\ (M) \longrightarrow CH_3\cdot\ (M) + CO_2$$
$$CH_3\cdot\ (M) + 2O \longrightarrow CO_2 + 3H^+ + 3e$$

(ii) that at pulse lengths greater than 10^{-3} sec, the normal Kolbe reaction resulting in the production of ethane and carbon dioxide proceeds, providing, one presumes, that at least the critical potential is attained in the pulse.

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[9] Normally Tafel slopes for the Kolbe reaction in the linear Tafel region are reproducible to 1 or 2 mv (*i.e.*, better than 1%) but may differ for ascending and descending directions of change of electrode potential, presumably on account of irreversibility of adsorption of species produced (including surface oxide in aqueous medium) in the reaction during the series of i/v measurements.

The principles involved in the mathematical treatment given by these authors (70) may be illustrated by means of a simple example for the reaction scheme

$$\mathrm{X} \underset{k_{7'}}{\overset{k_7}{\rightleftharpoons}} \mathrm{R}\cdot\ (\mathrm{M}) + \mathrm{e} \qquad \text{(Eq 7)}$$

$$\mathrm{R}\cdot\ (\mathrm{M}) \overset{k_8}{\rightleftharpoons} \mathrm{P} \qquad \text{(Eq 8)}$$

Assuming "Langmuir" conditions, *i.e.*, rate constants independent of coverage

$$\Omega \frac{\mathrm{d}\Theta}{\mathrm{d}t} = k_7 C_\mathrm{X}(1 - \Theta) - k_{7'}\Theta - k_8\Theta \qquad \text{(Eq 9)}$$

where Ω is the saturation coverage (moles cm^{-2}) of the surface. After solving for coverage Θ, they obtained

$$i = Fk_7C_\mathrm{X}\left(1 - (k_7C_\mathrm{X} + k_{7'}) \times \left\{1 - \exp\left[-\frac{\left(\frac{k_7C_\mathrm{X} + k_{7'} + k_8}{\Omega}\right)t}{k_7C_\mathrm{X} + k_{7'} + k_8}\right]\right\}\right) \qquad \text{(Eq 10)}$$

The integral yield of product P is given by

$$Y_t^P = \frac{1}{t}\int_0^t k_8\Theta \mathrm{d}t = \frac{k_7k_8C_\mathrm{X}}{k_7C_\mathrm{X} + k_{7'} + k_8} - \frac{k_7k_8C_\mathrm{X}\Omega}{(k_7C_\mathrm{X} + k_{7'} + k_8)^2}\frac{1}{t}\left\{1 - \exp\left[\left(-\frac{k_7C_\mathrm{X} + k_{7'} + k_8}{\Omega}\right)t\right]\right\} \qquad \text{(Eq 11)}$$

using the fact that $Y_{t=0}^P = 0$. Defining the relaxation time τ as $1/\tau = (k_7C_\mathrm{X} + k_{7'} + k_8)/\Omega$

$$Y_t^P = Y_\infty^P - Y_\infty^P \frac{\tau}{t}\left[1 - \exp\left(-\frac{t}{\tau}\right)\right] \qquad \text{(Eq 12)}$$

It may be noted that τ is determined by the largest rate constant. Equation 12 refers to the nonsteady-state yield.

The steady-state yield is given by

$$Y_\infty^P = k_8\Theta = \frac{k_7k_8C_\mathrm{X}}{k_7C_\mathrm{X} + k_{7'} + k_8} \qquad \text{(Eq 13)}$$

Equation 13 gives the limiting cases $(k_7k_8C_\mathrm{X}/k_{7'})$ and k_8 at low and at high coverage, respectively.

These authors applied this particular derivation to the complicated sequence of steps in the Kolbe reaction and obtained, after some approximations, the following equations.

For the nonsteady-state case

$$\frac{1}{\tau} \simeq \left(\frac{k_\mathrm{R}k_\mathrm{D}C_{\mathrm{A}^-}}{\Omega^2}\right)^{1/3} \qquad \text{(Eq 14)}$$

if the initial discharge *rate* $k_\mathrm{D}C_{\mathrm{A}^-}$ for the reaction

$$\mathrm{CH_3COO^-} \xrightarrow{k_\mathrm{D}} \mathrm{CH_3COO}\cdot\ (\mathrm{M}) + \mathrm{e}$$

is very much smaller than the *rate constant* k_R for the methyl radical recombination step, $2\mathrm{CH_3}\cdot\ (\mathrm{M}) \rightarrow \mathrm{C_2H_6}$. For the full quantitative definition of τ', the original paper may be referred to (70).

The product yield at short times, *i.e.*, before the steady state is established (*e.g.*, at pulse lengths $<10^{-3}$ sec), is given by

$$Y_t^P = \frac{k_\mathrm{R}k_\mathrm{D}^2C_\mathrm{A}^2 - t^2}{3\Omega^2} \qquad \text{(Eq 15)}$$

This yield may be compared with the one obtained under steady-state conditions, which is equal to $k_\mathrm{D}C_{\mathrm{A}^-}$.

In the derivation of Eq 14 and 15, the rates of the reverse steps of discharge and $\mathrm{CH_3COO}\cdot$ decomposition have been neglected. This, however, merits justification more substantial than the demonstrable irreversibility (very low i_0) of the over-all Kolbe reaction, since in treatments of consecutive processes the reverse steps cannot usually be ignored. It may also be pointed out that the equations derived by these authors do not give a good account of the experimental plots, a fact which the authors themselves have pointed out and discussed.

The following comments may be made about the mechanistic conclusions of these authors.

(i) Ethane is reported to be produced only under conditions of high coverage (experimentally observed) of the electrode by, it is claimed, methyl radicals (but there is no evidence presented against the possibility of acetoxyl radicals being the species predominantly covering the electrode); this, however, refutes the conclusion that initial discharge is the rds. If the latter conclusion were correct, the rate constant of this radical-producing step would necessarily have a much smaller value (after allowance for the proper units) than the rate constants of any subsequent bimolecular radical-removing steps that result eventually in ethane production. Under such conditions, the coverage of the electrode by radicals such as R· or RCOO· would tend to approach zero.

(ii) Estimations of the rate constants by these authors show that the initial discharge step has a value of the rate constant *greater* than that for the methyl radical recombination step. This would exclude the initial discharge as the rds. This particular criticism is not invalidated by the fact that the basis for estimating values of the rate constants involves some complicating uncertainties (which these authors acknowledge) since the difference in the values of the two rate constants reported seems to be beyond the range of anticipated errors.

(iii) The values of electrochemical rate constants both for the initial discharge and the recombination step reported in these investigations seem to be almost independent of the electrode potential, a result which is difficult to understand because the rate constant of the rds would normally tend to change by a factor of at least 10^2 over the interval of electrode potential reported (0.4 v).

(iv) It is proposed (70) that the Kolbe reaction proceeds only on the surface covered by an oxide layer. It will be shown below (section VI.A), rather unambiguously, that the Kolbe reaction can not only proceed on a surface *free* of oxide, but does so with greater efficiency than in aqueous media where coadsorbed surface oxide, being present, may inhibit, partially or completely, the Kolbe reaction and lead to the production of side products.

(v) There are also some qualitative discrepancies, it seems, between the theoretically expected current–time transients and the corresponding experimental plots reported in this work (70). Thus, as these authors themselves state (70), there are difficulties in obtaining quantitative information from these plots, particularly when both oxide and other electroactive adsorbed species are coadsorbed at an electrode surface.

(vi) A general matter arises in the repetitive pulse method in relation to (ii) and (iii) above insofar as, in the nonsteady-state, the relative coverages by intermediates will not usually be expected to be identical with the steady-state values; then, if interaction or heterogeneity effects are significant (27, 28, 157), the rate constants themselves will not necessarily be comparable with the steady-state rate constants. In extreme cases, relative magnitudes may even become changed and this may account for some of the difficulties mentioned in (ii) and (iii) above.

Finally, however, it must be stated that the work of Fleischmann, Mansfield, and Wynne-Jones, based on the earlier use of a pulse method by Lippincott and Wilson, has introduced a number of important new ideas and approaches into the study of the Kolbe reaction. The mechanistic conclusions of these authors must, however, be regarded as somewhat tentative at the moment, since the interpretations involve a number of assumptions which may not be kinetically justified for the conditions obtaining in the experiments.

3. *Other Recent Work on the Kolbe Reaction*

Fioshin and co-workers (65) electrolyzed a series of mixtures containing varying amounts of anhydrous H_2SO_4 and CH_3COOH. Small quantities of ethane were produced in the anode compartment when the solution contained not more than 50% H_2SO_4. Also, in another investigation (68; also see ref 66) the influence of the nature of the cation on the Kolbe reaction was examined and found to be of little significance in the part of the current–potential curve which represented the occurrence of the Kolbe reaction. However, in the part of the polarization curve that corresponded to oxygen evolution, a cation effect could be observed at low concentrations of the alkali acetate, *i.e.*, below 1 *N*. It was observed that the larger the cation radius, the lower the maximum current density for oxygen evolution and thus the higher the yield of ethane (at a given potential). Enlargement of cation radius is associated with an increase of the Tafel slope for the part of the polarization curve that (these authors suppose) corresponds to oxygen evolution.

Pande and Shukla (120) studied the Kolbe reaction in aqueous solutions of sodium salts of the paraffinic carboxylic acids. The current–potential curves were examined under galvanostatic conditions in formate, propionate, butyrate, caprylate, heptylate, and valerate solutions (1 *N*). Only sodium salts were examined and an aqueous medium was used. Characteristic breaks (*i.e.*, transition regions) were observed in the current–potential relations in all cases. Tafel slopes were not given and the current–potential plots were not related to the reaction mechanisms suggested on the basis of analyses of products of electrolytes. The Kolbe reaction in sodium acetate was not, however, studied. The mechanisms proposed by these authors were based solely on the nature of reaction products with little reference to the electrode processes, adsorbed intermediates, or kinetic behavior involved. Moreover, these authors seem to have overlooked all the relevant work on the Kolbe reaction done since 1936.

Another voltammetric study (2) of the Kolbe reaction has also been reported by Allen and co-workers. A number of aliphatic carboxylic acids were investigated voltammetrically in anhydrous CH_3OH at a rotating platinum anode. A $Hg–Hg_2(OAc)_2$ cathode was employed. No correlations between the structure and half-wave potentials were found to exist for the case of acids which yield Kolbe dimers. It was concluded that the formation of carboxylate radicals is potential dependent and the subsequent dimerization is only dependent on the resultant free-radical concentration on the electrode. This conclusion is consistent in a general way with the heterogeneous mechanisms involving radicals, described above. However, the dimerization kinetics may be influenced by anion specific adsorption and coadsorption of O species when water is present. Similar polarographic analyses were also attempted by some previous investigators (3). In general, it is unlikely that the oxidations are at all reversible so that the half-wave potentials have little quasi-thermodynamic significance.

The Kolbe reaction has also been examined on vibrating and on rotating platinum electrodes in sodium acetate solutions (66). The rate of reaction was found to be independent of the speed of rotation, so that the reaction between RCOO· or R· radicals must presumably be a heterogeneous one and the mass

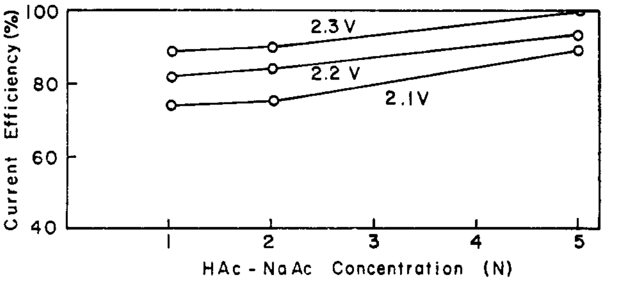

Figure 10.—Current efficiencies *vs.* concentration of electrolyte at each anode potential (after Sugino, Sekino, and Sato (151)).

transfer of initial reactant cannot be rate determining, as also indicated by the magnitude of i_0 values (35).

It was concluded that anions of the carboxylic acid become adsorbed at the oxidized surface of platinum and "anion–oxygen compounds of platinum" are formed (66). This suggestion is to be related to the known role of oxides in the Kolbe reaction, to be discussed in section VI.B.

Sugino and co-workers (139, 151) carried out potentiostatic studies on the Kolbe reaction, both in aqueous and nonaqueous media. These authors reported current–potential relations but not the usual log (current)–potential relations since their data did not extend over a wide enough current-density range; they also did not discuss the way in which these relations might be used in a diagnostic manner (*i.e.*, through interpretation of Tafel slopes and coverage effects) in determining the kinetic pathway and rds in the over-all reaction. The results of these authors were principally concerned with the analysis of the products formed under various experimental conditions (Figure 10). Similar comments also apply to the work of Leung and co-workers (112) who presented Tafel relations for the Kolbe reaction but did not make or discuss any kinetic conclusions. They also observed the characteristic transition region (26).

VI. Some General Problems Related to the Kolbe Reaction

In this section, some general problems will be examined, the understanding of which is desirable if any approach to a complete elucidation of mechanisms of the Kolbe reaction is to be made, especially when the reaction occurs in aqueous media.

A. ROLE OF COADSORBED (SURFACE) OXIDES IN AQUEOUS MEDIA

The role of surface oxides at Pt and Au electrodes in the electrolysis of aqueous acetate solutions was first investigated through studies of anodic charging curves by Dickinson and Wynne-Jones (42). These authors related the charge passed in anodic oxidation of the electrode surface to the critical conditions which they supposed were necessary for inhibition of the oxygen evolution reaction and promotion of Kolbe ethane synthesis. The quantities of anodic charge required to restore ethane evolution (A) and re-form the surface oxide layer (B) were also determined (Figure 6b), as a function of the length of periods of prior cathodic reduction of the surface.

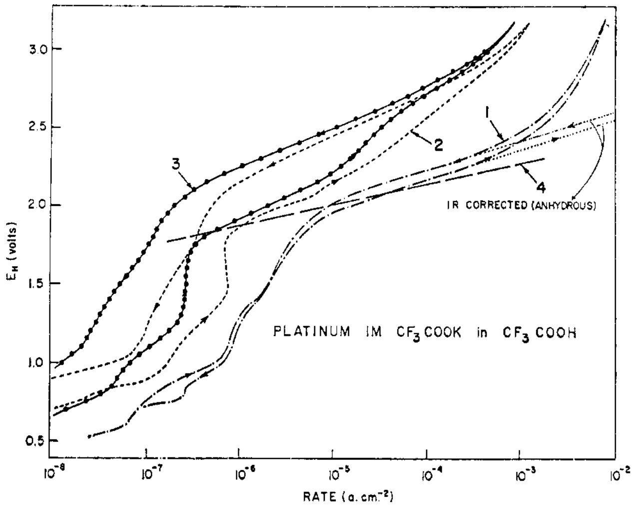

Figure 11a.—Steady-state (potentiostatic) current (*i.e.*, rate)–potential relations for Pt in 1 *M* CF_3COOK in CF_3COOH: (1) (— · —) very anhydrous solutions, b = 0.215 v; (2) (- - - -) "nominally" anhydrous solutions, b = 0.27 v; (3) (———) with added water, b = 0.25 v; and (4) (— —) Pt–1 *M* H_2SO_4, b = 0.14 v (after Vijh and Conway (163)).

A different approach was made by Conway and Vijh (31) who investigated the steady-state kinetic behavior in relation to the amounts of cathodically reducible oxide formed in the steady state at various potentials at Pt electrodes in anhydrous solutions, and in significantly and appreciably aqueous solutions. Their results may be examined best by considering several relevant figures.

In Figure 11a, potential–log (rate) relations for the Kolbe reaction at Pt in (a) *very* anhydrous 1 *M* KTFA–TFA (*i.e.*, 1 *M* potassium trifluoroacetate in trifluoroacetic acid) solutions prepared by addition of <1% trifluoroacetic anhydride to the chemically dried solvent, (b) in "nominally" anhydrous 1 *M* KTFA–TFA solutions, and (c) in aqueous 1 *M* KTFA/TFA solutions are compared (162, 163). It may be seen that at a given potential[10] the rate is the highest in the very anhydrous solution and lowest in the aqueous solution, with an intermediate value for the nominally nonaqueous one. The presence of water tends to give rise to a diminution of rate at a given potential. A similar conclusion may be drawn for the case of the

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(10) It has been shown in section V.A.1.d that the practical reversible potential for the Kolbe reaction, on the hydrogen electrode scale for the same solution, is the same in the aqueous or nonaqueous medium. Hence, comparisons of rates at a given numerical value of the measured potential under these conditions are legitimate and do not contain any unknown effects associated with different potential scales. The comparisons are, in effect, therefore, being made at the *same overpotentials*.

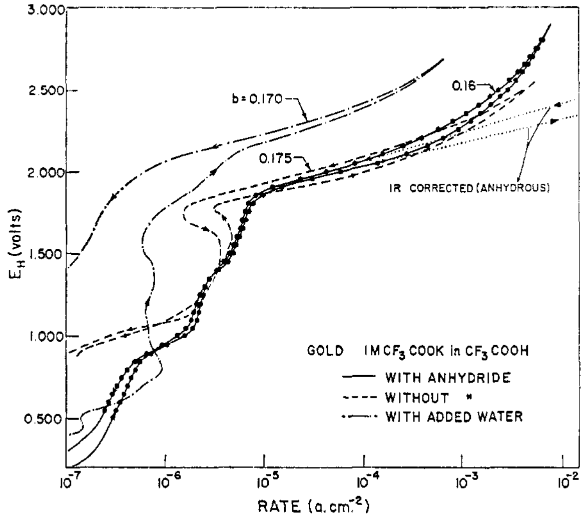

Figure 11b.—Steady-state (potentiostatic) current (*i.e.*, rate)–potential relations for Au in 1 *M* CF_3COOK in CF_3COOH: (1) (———) very anhydrous solutions, (2) (. . . .) "nominally" anhydrous solutions, and (3) (– – – –) aqueous solutions. Note: A typical population of experimental points and a typical correction for resistance effects (*IR* drops) have also been shown both in the (a) and (b) figures (after Conway and Vijh (31)).

Kolbe reaction at gold in TFA solutions (Figure 11b) (31).

Any surface oxide[11] on Pt, if present, may be detected by means of a constant current cathodic reduction transient over a time interval of 0.1–10 msec. That the reduction is of a surface species may be shown by demonstrating that the transition time for the reduction is inversely proportional to the cathodic current density (33), and that the capacity profile has the normal shape for reduction of an adsorbed species (27, 28, 79).

In Figure 5, four oscilloscope photographs are shown; three of these represent the electrochemical reduction behavior of the species adsorbed on the platinum electrode surface in the course of the Kolbe reaction proceeding under prior steady-state conditions. The curves, and their differentiated profiles, represent the time dependence of the potential of the electrode at which the Kolbe reaction was taking place previously in a steady state, during reduction at a constant current density *i* from anodic potentials previously maintained constant by a potentiostat. The profiles in Figure 5 (1–3) are for the three types of trifluoroacetate solution studied; the fourth photograph (Figure 5 (4)) shows, for comparison, the transient for the adsorbed species (which can only be surface oxide) formed anodically in aqueous H_2SO_4 alone. The arrests, Δt, which are seen in the transient (or minima and maxima in the corresponding differentiated profiles) indicate the presence of electroactive adsorbed intermediates, and the charge required for their reductive removal is given by $i\Delta t$ (98). It may be seen that no arrests are apparent when completely nonaqueous solutions are used; there is a short arrest for the case of nominally anhydrous solution, demonstrating reduction of small amounts of electrochemically formed oxide (or adsorbed O-containing species) originating from the traces of water present in this solution through the reactions mentioned in footnote 11. There is a large arrest under aqueous solution conditions, indicating appreciable coverage by adsorbed species, *e.g.*, oxide arising again from the water in the aqueous solution. That these species may be identified with surface oxide is indicated among other more indirect evidence (see section IV.B.3) by the fact that the potential range over which the reduction occurs is almost identical with that over which a corresponding reduction occurs in aqueous H_2SO_4 or $HClO_4$ media where only oxide can be present on the surface (4, 82).

From the foregoing discussion, the following may be concluded: an increase in the concentration of water in the solution gives rise to increasing amounts of a cathodically reducible adsorbed species and to decreasing rates of the electrode reaction at a given anodic potential. Hence, it must be concluded that water is the likely source of the electrochemically adsorbed species which diminish the rate of the Kolbe reaction; the latter, like all electrode processes, proceeds heterogeneously at the metal interface, and its rate (and possibly its mechanism) is subject to changes caused by coadsorbed species formed from the solvent (4, 85).

The foregoing conclusion also holds for the case of the Kolbe reaction proceeding at gold in the three types of solution studied. In Figure 12a, a family of plots is presented; each one of these relations refers to a given value of electrode potential over the potential range in which the Kolbe reaction is known (from product yield studies) to occur (*i.e.* >2.1 v E_H). Each individual plot represents a rate (measured from kinetic current–potential curves) *vs.* charge Q (calculated from the differentiated cathodic transients) relation at a given potential, for three points, where each point corresponds, respectively, to results obtained for the three solutions studied. It may be seen that at any potential, as conditions are changed from those corresponding to "very anhydrous" to those corresponding to "nominally anhydrous" and then to "aqueous solutions," the

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(11) The nature of the oxidized Pt anode surface above about 0.8 v E_H in water-containing solutions is a matter of quite general importance in anodic reactions. It appears that initially an adsorbed species such as OH or O arising from water by reactions such as $Pt + H_2O \rightarrow Pt/OH\cdot + H^+ + e \rightarrow Pt/O + H^+ + e$ may be present. A possible interpretation of the ellipsometric evidence (132) indicates transformation to a two-dimensional phase oxide above about 1.0–1.1 v, an effect which is undoubtedly connected with the intrinsic irreversibility of the processes of anodic formation and cathodic reduction of the oxide at Pt. Physically, this transformation (and the associated hysteresis) may be envisaged as involving migration of the O and Pt atoms in such a way as to make a two-dimensional "Pt–O" lattice from an initially formed Pt–O dipolar layer. The hysteretic effect suggests that the surface oxide is formed in metastable domains (53) which undergo an irreversible phase transition so that the oxide is reduced only at a lower anodic potential than that required for its formation. For simplicity, therefore, we shall refer here and elsewhere in this review to the oxygen species at the Pt anode as "oxide" or "surface oxide."

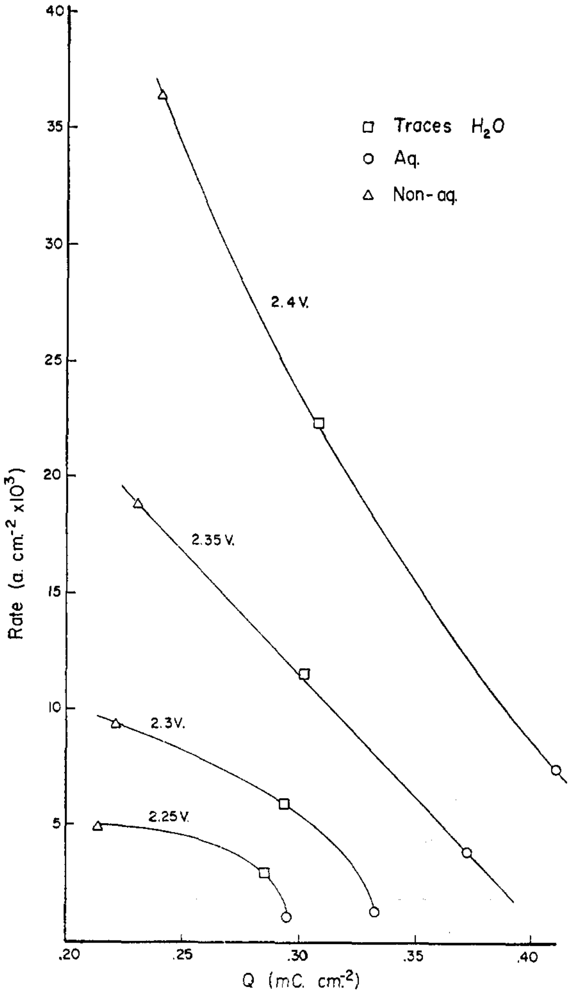


Figure 12a.—Gold in 1 *M* CF_3COOK in CF_3COOH: plots of cathodic charge of *Q vs.* rate at various anodic potentials for completely anhydrous (△), nominally anhydrous (□), and aqueous solutions (○) (after Vijh and Conway (163)).

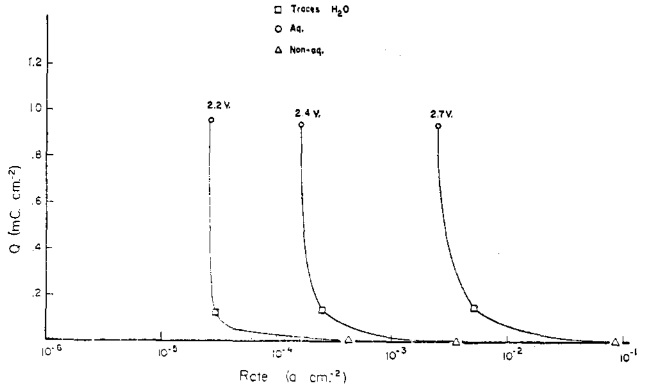


Figure 12b.—Platinum in 1 *M* CF_3COOK in CF_3COOH: plots of cathodic charge of *Q vs.* rate at various anodic potentials for completely anhydrous (△), "nominally" anhydrous (□), and aqueous solutions (○) (after Vijh and Conway (163)).

charge *Q* for the cathodic reduction of species on the surface increases, but the corresponding electrochemical rates decrease. This again indicates that increasing amounts of adsorbed intermediates, presumably the surface oxide, arise from increasing amounts of water present in the solution, and the presence of this surface or adsorbed oxide results in a corresponding decrease in reaction rate. However, quantitatively, the charge associated with oxide coverage in the Kolbe reaction, both with CF_3COOK and potassium acetate in aqueous acetic acid, is substantially lower than that observable when the electrode is anodically polarized in aqueous sulfuric acid alone. Figure 12b shows similar effects on platinum in CF_3COOH solutions (*cf.* Figure 4).

A related effect is observed in aqueous medium containing 0.1 *M* H_2SO_4, where successive additions of CF_3COOH up to 3.5 *M* cause a progressive decrease in the oxide reduction peak at Pt when potentials are scanned between +0.015 and +1.7 v E_H. The oxide formation region is also changed a little in shape. If, however, scans are made up to *ca.* 3.5 v, the oxide reduction peak becomes larger (by *ca.* 20%) than that for aqueous H_2SO_4 above, and its maximum is observed at some 0.15 v more cathodic than in the case of aqueous H_2SO_4 solutions alone. A similar effect was noted in the case of the acetate Kolbe reaction by Dickinson and Wynne-Jones (42). The increase of oxide coverage which is evidently induced by polarization at very high potentials (3.5 v) may be simply connected with the fact that the electrode field, which can then be attained when the Kolbe reaction is proceeding, is substantially larger than that attainable at practical current densities in aqueous H_2SO_4 solutions alone, where the anodic process of O_2 evolution is much more facile. The oxide reduction peaks at Pt in aqueous CF_3COOK in 0.01 *N* CF_3COOH taken from various anodic potentials are compared in Figure 13 in which it will also be noted that a marked inhibition inflection region (*cf.* Fioshin and Vasil'ev (67)) is exhibited at quite high anodic potentials (3.0 v) with a second minor peak at 3.3 v. The current peak is not a charging peak but rather a true kinetic inhibition peak, since the peak current is maintained under steady-state conditions (Figure 13). The inhibition of the process at the current maximum cannot originate from the formation of surface oxide (*cf.* ref 85) since the latter is already laid down by 1.6 v E_H; however, the inhibition may arise from intermediates formed in the Kolbe process itself or by a change of chemical catalytic properties of the surface oxide at high potentials as it grows somewhat thicker at high surface fields.

Finally, with regard to the role of water in solution in relation to inhibition effects, the presence of water is not only not necessary for the Kolbe reaction to proceed but in fact evidently leads to significant inhibition effects. This is also borne out by yield studies where the best yields of R_2 [96% in the case of CF_3COOK giving C_2F_6 (25)] are usually obtained in a nonaqueous medium (54); *e.g.*, the anhydrous acid itself (when a liquid) containing its own salt as electrolyte

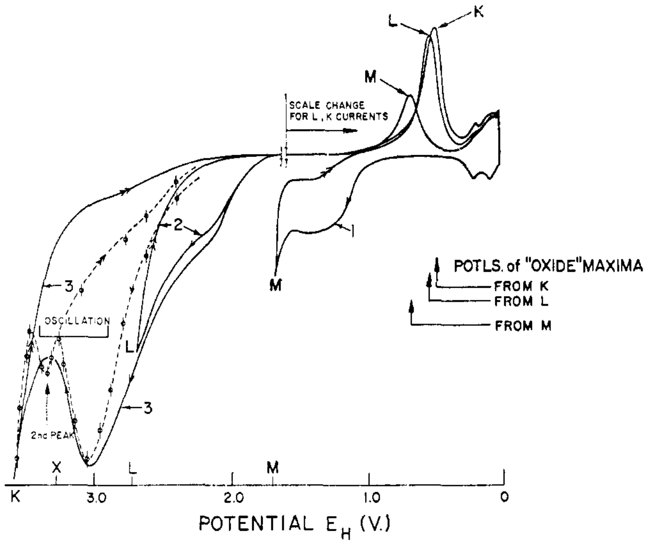


Figure 13.—Potentiodynamic current–potential relations for CF_3COOK in aqueous 0.01 *N* CF_3COOH solution at Pt (25°), showing (a) oxide reduction region for electrode taken previously to various high anodic potentials in the pre-Kolbe (curve 1) and Kolbe region (curves 2 and 3); (b) kinetic inhibition reversal effect at high anodic potentials (curve 3); and (c) kinetic inhibition reversal effect under steady-state (20 sec per point) conditions (dashed line) (note presence of *two* kinetic inhibition regions close together at *ca.* 3.0 and 3.3 v E_H). Compare Figure 8a with regard to the acetate reaction.

is often the preferred medium for execution of a Kolbe coupling reaction.

The conclusion made above that surface oxides are coadsorbed together with Kolbe adsorbed species in aqueous media receives some complementary corroboration from potentiodynamic profiles, *e.g.*, Figures 4a and b. Potentiodynamic profiles are reproduced in Figure 4a in which charging peaks on platinum in potassium acetate and sulfuric acid solutions are compared. The general similarity of the shapes of the peaks, and the potentials at which they appear, strongly suggest that the peaks for the acetate solutions are "modified" peaks for oxygen and hydrogen deposition and desorption processes. Similar results are found for trifluoroacetate solutions, as described above (Figure 13). The profiles in Figure 4a may also be compared, for identification purposes, with the schematic diagram in Figure 4b.

If Q_0 is the charge for the oxide reduction peak in the potentiodynamic profile (*i.e.*, the area $\int i dt$ under the curve) and Q_H is the charge for the hydrogen deposition peak, it has been observed that the ratio Q_0/Q_H (=1.5) for the case of platinum in aqueous, acidic CH_3COOK solutions is noticeably lower than the ratio Q_0/Q_H (=2.4) for the case of platinum in sulfuric acid (162, 164). Since the ratio Q_0/Q_H for platinum in H_2SO_4 is increased by 58% over that for platinum in acetate solutions, it may be concluded that in aqueous, acidic, acetate solutions the surface coverage associated with the peak with $V_{C_{max}} = 0.55$ v refers to species which are on the average bulkier than the oxide; *e.g.*, $CH_3COO\cdot$ coadsorbed with oxide may be the species involved. An alternative explanation of this decreased Q_0/Q_H ratio for the acetate solution may be that only a part of the surface is covered by oxide and a part of it is bare; however, it is impossible to conceive of a partially bare electrode at the high anodic potentials reached in the Kolbe reaction. The possibility of $CH_3\cdot$ being a probable substantially adsorbed species is excluded on the basis of arguments developed elsewhere (164).

B. SIDE PRODUCTS. ORIGIN AND MECHANISM OF FORMATION

The existence of the surface oxide may also have a bearing on conclusions which have been made regarding the origin of carbonium ions (37, 45, 49, 130, 167) in the Kolbe reaction as deduced from the nature of side products. Thus, products such as alcohols ROH (Hofer–Moest reaction), which can be formed, might arise, it seems, just as well from steps involving heterogenous oxidation of adsorbed R· radicals by the Pt surface oxide as from anodic ionization to form R^+ and subsequent rapid reaction with the solvent or electrolyte anions. Such processes may be represented as follows, but clear exceptions involving rearrangements characteristic of carbonium ion intermediates must be recognized, as discussed below.

$$RCOO^- \xrightarrow{-e} RCOO\cdot\,(M) \xrightarrow{-CO_2} R\cdot(M) \begin{cases} \xrightarrow{-e} R^+ \text{ (direct electrochemical)} \\ \xrightarrow[+H^+]{+PtO} R^+ + PtOH \text{ (via oxide)} \end{cases}$$

followed by

$$R^+ \begin{cases} \xrightarrow{H_2O} ROH + H^+ \\ \xrightarrow{OH^-} ROH \end{cases}$$

or

$$R^+ + R'COO^- \longrightarrow R'COOR$$

The latter process could account for the observed production of small amounts of esters.

Alternatively, direct heterogeneous oxidation by steps such as

$$Pt/OH + Pt/R\cdot \longrightarrow ROH$$

or

$$Pt/OH + Pt/RCOO\cdot \longrightarrow ROH + CO_2$$

could account for production of some of the side products, as pointed out by Dickinson and Wynne-Jones (42). In other cases of more complex molecules where special products arise which could originate only from carbonium ions, the case for the involvement of the latter is stronger, *e.g.*, in the work of Corey and Bauld (36, 38) with *endo*- and *exo*-norbornane-2-carboxylic acid. The direct involvement of surface oxides may, in certain cases, be important because of their possible role in the parallel reactions.

The formation of alcohol ROH instead of the Kolbe coupling product R_2, possibly *via* a carbonium ion pathway, is known as the Hofer–Moest reaction (88, 99). When the Kolbe reaction is the major process, formation of ROH occurs only as a minor side product and may also account for the presence of trace amounts of other side products, *e.g.*, aldehydes (70) through a further oxidation of the type

$$R'{-}CH_2{-}OH \longrightarrow R'CHO \longrightarrow R'COOH$$

Experimentally, products of oxidation of the entity R usually originate at *lower* anodic potentials than those at which the Kolbe reaction proceeds with the optimum efficiency in aqueous media. It could therefore be argued that these side products do not normally originate by a carbonium ion pathway since carbonium ions would tend to be preferentially formed both for kinetic and thermodynamic reasons at higher, rather than lower, positive potentials. However, this suggestion cannot be supported by any experimental evidence and the proposals given below seem preferable.

We may suppose that the apparent necessity for high anodic potential (*cf.* section VI.D) to be attained before the Kolbe reaction proceeds efficiently is associated, in part, with the coverage Θ_R required for recombination to proceed at a rate sufficiently competitive with any side oxidation reactions such as

$$R\cdot/M \longrightarrow R^+ \text{ or } R\cdot/M + PtOH \longrightarrow ROH$$

Obviously recombination will usually proceed at a rate proportional to $\Theta_R{}^2$ while any side reactions, *e.g.*, as shown above, will proceed at rates proportional to Θ_R. (Desorption and *homogeneous* recombination of R will usually tend to be relatively inefficient processes; see section III.D.) The side reactions will therefore tend to be preferred (on a coverage basis) except at higher coverages, or if the activation energy for recombination favored the latter process. In general, the coverage Θ_R will be an approximately exponential function of electrode potential V if R is formed directly or indirectly through an ion-discharge process, so that depending on the relative values of rate constants for the forward and backward directions of prior ion discharge and radical decarboxylation steps, values of Θ_R sufficiently large for the side reactions to be no longer predominant may simply not arise until relatively high anode potentials (>*ca.* 2.2 v) are attained.

Olefins and paraffins possessing only half the number of carbon atoms of the normal Kolbe product are favored as side products at low anodic current densities (143). This is probably due to the fact that at low current densities, a sufficiently high steady-state coverage of the electrode for promoting the Kolbe coupling efficiently is not yet achieved, and an abstraction reaction (*cf.* Clusius (19)) of the following type occurs.

$$CH_3\cdot + CH_3COO^- \longrightarrow CH_4 + \cdot CH_2COO^-$$

or (less likely) through

$$CH_3\cdot + CH_3\cdot \longrightarrow CH_4 + CH_2\colon$$

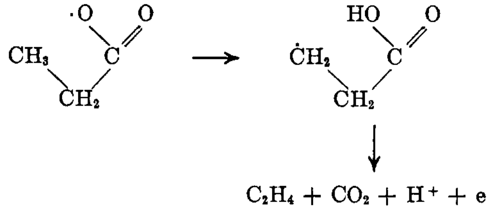
followed by

$$2CH_2\colon \longrightarrow C_2H_4$$

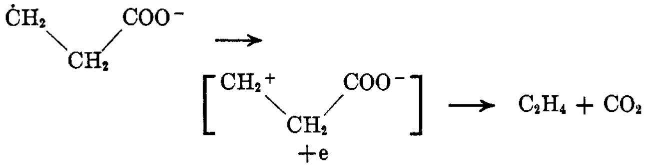
However, particularly when propionate is used as the starting material, the olefin C_2H_4 is formed together with some butane. This suggests that following the initial discharge to form adsorbed $CH_3CH_2COO\cdot$ radicals, either hydrogen abstraction between $CH_3CH_2\cdot$ occurs (following heterogeneous decarboxylation), *viz.*

$$2CH_3CH_2\cdot \longrightarrow C_2H_4 + C_2H_6$$

in preference to coupling, or, less likely, an internal hydrogen migration with propionate could account for the observed production of C_2H_4.



or



The following alternative pathways seem more satisfactory possibilities.

(from propionate)

$$C_2H_5\cdot + CH_3CH_2COO\cdot/M \longrightarrow C_2H_6 + C_2H_4 + CO_2$$

(from acetate)

$$CH_3\cdot + CH_3COO^- \longrightarrow CH_4 + \cdot CH_2COO^-$$

$$2\dot{C}H_2COO^- \longrightarrow {}^-OOCCH_2CH_2COO^- \longrightarrow 2CO_2 + C_2H_4 + 2e$$

Thus, succinic acid is known to form C_2H_4 under "Kolbe" oxidation conditions. The above mechanisms are, however, largely speculative at the moment. The disproportionation reaction giving C_2H_6 and C_2H_4 from propionate is not, however, general since longer chain aliphatic carboxylates do give largely the expected Kolbe hydrocarbon (120) as is also the case with monoesters of dicarboxylic acids (Crum-Brown–Walker synthesis). The ratio of disproportionation to recombination products has been discussed in section III.C.2.

In relation to the above mechanisms, the failure of the Kolbe reaction to occur with benzoate is of interest. For this case, the principal product is benzene instead of the expected biphenyl. Presumably again hydrogen abstraction is the preferred pathway, reflecting the expected high energy and reactivity of the phenyl radical, *e.g.*, as indicated by the formation of phenylation products in the course of the "Kolbe" reaction with benzoic acid in pyridine (59) where phenylpyridines and diphenyl-4-carboxylic acid are products.

Esters of the initial reactant acid have sometimes been observed as side products and could arise by reaction of the Hofer–Moest product ROH with the parent acid RCOOH as follows.

$$ROH + RCOOH \longrightarrow RCOOR + H_2O$$

Alternatively, esters could also arise, perhaps more probably, by the following sequence of reactions (1, 169).

$$RCOO^- \xrightarrow{-e} RCOO\cdot\ (M) \xrightarrow{-CO_2} R\cdot\ (M)$$

$$R\cdot\ (M) + RCOO^- \xrightarrow{-e} RCOOR$$

or

$$R\cdot\ (M) + RCOO\cdot\ (M) \longrightarrow RCOOR$$

The carbonium ion pathway could also lead to ester formation as mentioned above.

In distinction to some of the conclusions made above regarding the role of carbonium ions in side product formation in the Kolbe reaction at Pt, an important contribution by Koehl (103, 104) has given positive indications of carbonium ion intermediates in the electrolysis of carboxylic acids at *carbon* anodes. From acetic acid, methyl acetate is formed in 82% yield; from butyric acid, propene and cyclopropane (142) are formed in a 1:2 ratio together with *n*- and isopropyl butyrate, also in a 1:2 ratio. Under similar conditions at Pt, Kolbe coupling is the predominant reaction. In a number of special cases, the failure of the Kolbe reaction to proceed efficiently can be related (37) to the stability of known carbonium ions that may be formed as a result of anodic oxidation of the R function; this may also be the case with α-substituted carboxylic acids (except CF_3COOH) which usually give poor yields of Kolbe dimers (174a). In the case of simple, unsubstituted acids, the reasons for carbonium ion formation are less clear. It might be suggested that the indication of their formation at carbon anodes and not at Pt is connected with the absence of a phase surface oxide at carbon and the different energetics of chemisorption of R· and RCOO· radicals at the carbon and oxidized platinum surfaces. It is thus reasonable to suppose that at Pt, alkyl radicals will be stabilized by chemisorption while at carbon an oxidative desorption to form carbonium ions and consequent products will tend to be a preferred pathway. Similarly, the superior catalytic properties of Pt will tend to promote recombination of the adsorbed alkyl radicals in preference to desorptive oxidation.

The production of carbonium ions is envisaged as

$$\begin{tikzcd} RCOO^- \arrow[r] & RCOO\cdot + e \arrow[dr] & & \\ & & R\cdot + CO_2 \arrow[dr] & \\ & & & R^+ + e \end{tikzcd}$$

or from RCOO· by

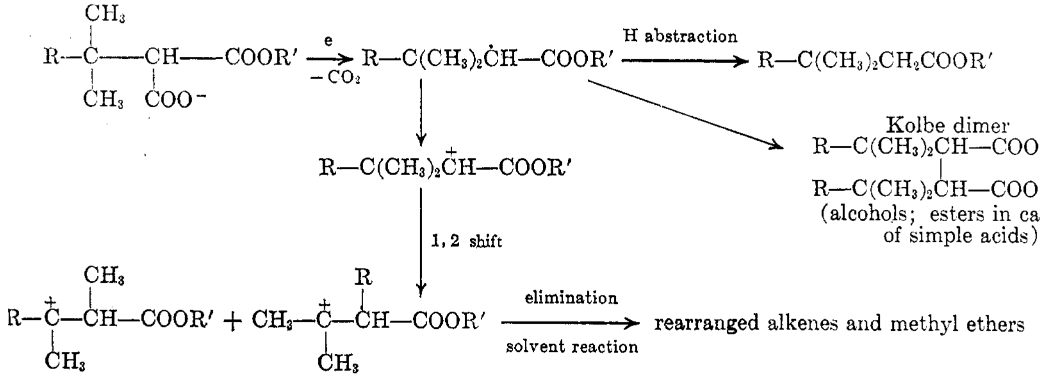
$$\begin{tikzcd} RCOO\cdot \arrow[r] & RCOO^+ + e \arrow[dr] & \\ & & R^+ + CO_2 \end{tikzcd}$$

In the case of anodic electrolysis of pentanoic acid (103), the products are very similar to those arising from the deamination (149, 156) of butylamines and the deoxidation (142) of butyl alcohols. For the latter two cases, the intermediates are accepted (148) as being *n*-butyl carbonium ions, and, for all three cases, very similar proportions of butene isomers are produced. With acetic acid, methyl acetate is formed to appreciable extents in both aqueous and anhydrous solutions. This suggests that in the former case (where, in fact, the ester yield at carbon is surprisingly greater in the aqueous than in the anhydrous medium) the methyl carbonium ions, if formed, react preferentially with acetate ions or acetic acid molecules adsorbed in the double layer at the electrode *interface;* otherwise methanol would be expected to be the predominant product from reaction of CH_3^+ with excess H_2O, as it is at Au electrodes (169). Finally, it must be remembered that methyl acetate may also be formed (as mentioned above) directly from $CH_3\cdot$ and $CH_3COO\cdot$ radicals without the involvement of any carbonium ions. The fact that the yields of methyl acetate at carbon in aqueous and anhydrous acetic acid are not radically different reinforces this conclusion. This, however, does not seem to be the case with the more complex higher acids for the reasons quoted above.

The reactions discussed here indicate again the necessity for considering anodic decarboxylation reaction mechanisms very specifically with regard to electrode material, solvent, and potential.

In order to demonstrate the competition between free radical and carbonium ion processes in anodic electrolysis of selected carboxylic acids, Eberson and Sandberg (50) investigated the course of the Kolbe reaction at Pt in methanolic solutions using α-alkoxycarbonyl acids, *t*-alkylmalonic half-ester anions of the type $RC(CH_3)_2CH(COOR')COO^-$. These compounds are ideal for studying the distribution between radical and carbonium ion products as there are no H atoms on the C atom β to the carboxyl group. Reasonably good Kolbe yields of the respective dimers were obtained with compounds where $R = C_2H_5$ (74%), SCHEME I

SCHEME OF EBERSON (50) FOR VARIOUS SUCCESSIVE REACTIONS IN ELECTROLYSIS OF CERTAIN HALF-ESTERIFIED DICARBOXYLIC ACIDS



R = alkyl or phenyl; R′ = alkyl

C_3H_7 (71%), i-C_3H_7 (76%), and CH_3 (85%), while with R = C_6H_5, yields were lower (48%). Side reactions to give carbonium ion products are indicated when the intermediate free radical has an ionization potential appreciably below 8 ev. This value, however, seems rather high, and we must note that solvation factors should be taken into account as well as the ionization potential in considering the conditions under which carbonium ions are likely to be formed. Attention is also directed by Eberson and Sandberg to the role of (a) disproportionation of radicals and (b) H abstraction (see section VI.B.) from solvent or solute molecules, as well as to the various rearrangements which may result from the production of carbonium ions. A scheme of reaction pathways (Scheme I) is given based in part on Eberson's paper; the identity of the actual products formed depended on the chemical nature of R and R′.

In some cases, ketones (105, 125) may arise as minor side products presumably through a further anodic oxidation of the Hofer–Moest product ROH, *e.g.*, as might be the case with R = $(CH_3)_2CH$– from isobutyric acid. Aldehydes would arise from normal aliphatic acids by a similar mechanism.

Dimethyl peroxide has also been observed in traces as a side product in the Kolbe reaction on platinum in aqueous acetate solutions. It has been suggested that the coupling of two methyl radicals with the oxygen diradical is the source of dimethyl peroxide, but details have not been given (70). The possible involvement of diacetyl peroxide has been referred to earlier (section III.A).

Whereas the Kolbe reaction proceeds with good yields in the case of trifluoroacetate in aqueous and nonaqueous media at platinum, the α-monohalo acids are reported not to undergo the Kolbe reaction. Similarly, α,β-unsaturated acids also fail to give the corresponding Kolbe hydrocarbon (polymerizations are usually involved); dicarboxylic acids also fail to undergo the Kolbe reaction but their monoester salts can be made to dimerize with decarboxylation: this is an important procedure for chain extension. Details of the chemistry involved in these cases have been given in previous reviews where tabulations of various side products formed have also been presented.

C. A POSSIBLE OXIDE PATHWAY FOR THE KOLBE REACTION IN AQUEOUS MEDIA

The following oxide pathway (35, 162) must be noted as a possibility since the presence of appreciable adsorbed surface oxide has been observed in the range of potentials over which the Kolbe reaction occurs in aqueous reaction media (25, 42, 70, 162, 164). Instead of a direct acetate ion discharge step, it is possible to write a heterogeneous chemical oxidation of the type

$$\text{"PtO"} + CH_3COO^- + H^+ \longrightarrow CH_3COO\cdot\ (M) + \text{"PtOH"} \qquad (F)$$

with "PtO" formed from the aqueous medium by electrochemical steps such as

$$Pt + H_2O \longrightarrow \text{"PtO"} + H^+ + e$$

or alternatively to (F)

$$\text{"PtO"} + CH_3COOH \longrightarrow CH_3COO\cdot\ (M) + \text{"PtOH"} \qquad (G)$$

where "PtO" and "PtOH" are nominally sites of higher and lower degrees of surface oxidation at the Pt electrode interface but not necessarily of the stoichiometry formally indicated. The species $CH_3COO\cdot$ (M) may then undergo further reactions down the sequence of steps of type C and types D, D′, and D″ or E (see section IV.A.1). The continuous anodic *electrochemical* process involved would be steady-state reoxidation of "PtOH" to "PtO" by the step

$$\text{"PtOH"} \longrightarrow \text{"PtO"} + H^+ + e \qquad (H)$$

which could be coupled with (F) or (G) in the steady state.

This scheme is regarded as an unlikely pathway since (a) the Kolbe reaction proceeds in nonaqueous media with rather similar electrochemical kinetic characteristics to those for the reaction in aqueous media; hence a radically different mechanism is unlikely in aqueous media (31, 34); (b) it proceeds at a *faster* over-all rate in nonaqueous media than in aqueous media, other things being equal (Figures 11a and 11b (31, 163); and (c) no gas evolution can be detected in a differential manometer cell when an aqueous CH_3COOK–CH_3COOH mixture is treated with platinum dioxide (35, 162).

D. INHIBITION OF THE OXYGEN EVOLUTION REACTION AND RELATED PROBLEMS

It has been pointed out above that the presence of coadsorbed surface oxide on the electrode, originating from traces or excess of water in the solutions, can result in partial inhibition of the Kolbe reaction (section VI.A). However, the important and related question (88–91, 97) of why the Kolbe reaction usually proceeds in *preference to oxygen evolution* in aqueous acetate solutions on Pt or Ir at higher potentials (*ca.* >2.2 v) (97) we have not yet considered. The possible discharge of OH radicals in preference to acetate at low potentials has been noted (42), but the reasons why a change of electrode process should occur as the potential is raised have not received adequate quantitative consideration. Normally, at high anodic potentials in aqueous media, oxygen would be evolved at relatively high rates in the absence of carboxylate salts. Here we examine possible factors involved in inhibition of oxygen evolution when "Kolbe" reactants are present.

1. *Inhibition of Oxygen Evolution: Some Hypotheses*

It has been suggested by Dickinson and Wynne-Jones (42) and by Eberson (46) that discharged acetate species (42), or a chemisorbed layer (46, but note that this author did not consider this chemisorption in his thermochemical calculations), block the oxygen evolution process and hence favor the Kolbe coupling. In relation to these proposals, it has been concluded above that an effective (dipole) barrier-layer of RCOO· radicals (Figure 2) may exist coadsorbed with oxide (see section VI.A) on the Pt electrode when the Kolbe reaction itself is proceeding, but would also have a similar effect in any potential-dependent discharge of species from water to form oxygen. The Tafel slope for such a process involved in oxygen evolution would thus be raised, so that at the high potentials at which the Kolbe reaction proceeds at moderate or high rates, the oxygen evolution reaction itself would hence proceed only much more slowly than it would (at those same potentials) in the absence of the Kolbe species (162, 164). Thus the efficiency of the Kolbe reaction would tend to be higher than would be expected by comparison between the Tafel parameters for the two reactions considered separately. This is schematically represented in Figure 14 where KK′ is the Tafel line for the Kolbe reaction; OO is the normal Tafel line for the oxygen evolution reaction, *i.e.*, in the absence of a dipole barrier-layer film of adsorbed radicals (*e.g.*, for Pt in H_2SO_4), and OO′ is the expected Tafel line for the oxygen evolution reaction in the presence of a dipole-layer film of adsorbed RCOO·. It may be seen that at potentials higher than those represented by point C (the crossing point of KK′ and OO′) the Kolbe reaction would be the preferred process (162, 164). In the absence of such an effect, it is difficult to explain why oxygen evolution should not be the major process at higher potentials on Pt or Ir in aqueous acetate solutions (97), when the normal Tafel line for the oxygen evolution reaction in acid solution (*i.e.*, in the absence of any films giving barrier-layer type effects) commences at a lower potential and has a lower slope than the one for the Kolbe reaction (see Figure 11a) (163).

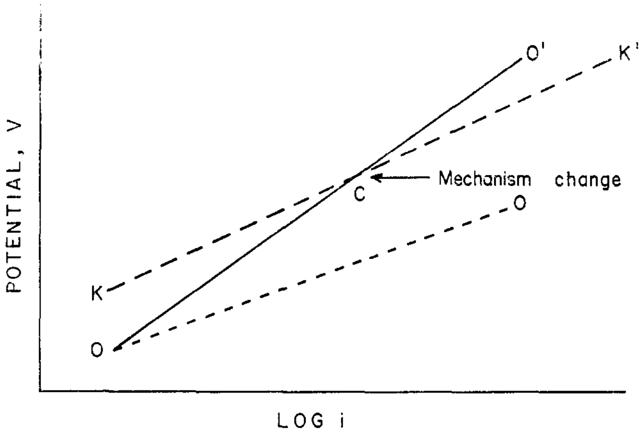


Figure 14.—Schematic representation of current–potential relations leading to inhibition of the oxygen evolution reaction at high anodic potentials in aqueous CF_3COOK solutions at Pt (after Vijh and Conway (164)).

A second effect may arise from the influence of one adsorbed species on another and on the kinetics of the two processes tending to occur simultaneously. Thus, coadsorbed RCOO· species ("substituted" surface oxide) may change the energy of adsorption of intermediates "OH" or "O" in the oxygen evolution reaction (7). Two types of effect may then arise: (i) the steady-state coverage of such species may be modified and hence the rate of the oxygen evolution reaction could become changed; and (ii) the presence of coadsorbed species such as RCOO· may raise the activation energy for steps in the oxygen evolution reaction, *e.g.*, by weakening bonding of the species adsorbed in the latter process to the surface (27).

A second hypothesis has been proposed by Fioshin and Vasil'ev (66, 67) and involves the effect of adsorbed (acetate) anions in modifying the kinetics of the oxygen evolution reaction. According to these authors, inhibition of oxygen evolution results because of the specific adsorption of acetate ions; this causes reduction in the surface concentration of water molecules (or hydroxyl ions) and therefore results in suppression of the oxygen evolution reaction; *i.e.*, this is basically a concentration effect which decreases the rate of the oxygen evolution reaction without, it may be pointed out, necessarily affecting the rate constant and the potential profile at the metal–solution interface. The hypothesis of Vijh and Conway (162, 164), and Dzieciuch and Conway (25), on the other hand, involves a model where the presence of a film of chemisorbed *radicals* on the electrode surface changes the profile of the potential drop across the metal–solution (but now metal-film–solution) interface and retards the oxygen evolution reaction by causing an apparent decrease in the value of rate constants (or correspondingly by augmenting the activation energy) for steps in the oxygen evolution reaction.

A kinetically significant extent of specific adsorption of acetate ions does not appear to be sustained by the following experimental observations.

(i) Increased specific adsorption at higher concentrations of acetate ions would imply lower rates at a given potential for the oxygen evolution; *i.e.*, an increase in the Tafel slope, b, for oxygen evolution, up to anomalous values would be expected, as indeed is observed. However, the anomalous Tafel slopes which are observed for the Kolbe reaction itself are difficult to explain on the basis of the hypothesis of Fioshin and Vasil'ev (66, 67) but seem to be more readily interpreted in terms of the considerations suggested by Vijh and Conway (162, 164) as discussed below.

An alternative and more general type of explanation for high Tafel slopes in relation to time effects has been given by Busing and Kauzmann (16) in terms of progressive poisoning or deactivation of a distribution of active sites on the electrode surface. This approach probably justifies some more detailed consideration in the case of the Kolbe reaction where unusually high Tafel slopes are an intrinsic characteristic of the reaction kinetics and do not arise adventitiously from the presence of impurities as they do sometimes in the case of the cathodic hydrogen evolution reaction.

(ii) The ratio Q_O (charge for oxide reduction)/Q_H (charge for hydrogen deposition) would be expected, to a first approximation, to be independent of specific adsorption effects. It has been observed that the ratio Q_O/Q_H for the case of platinum in aqueous, acidic acetate solutions is, however, substantially smaller than the same ratio for the case of platinum anodes polarized in sulfuric acid alone (162, 164). This suggests that in the case of the acetate solutions some species other than surface oxide, and bulkier than the latter, is coadsorbed together with the surface oxide; *i.e.*, an appreciable coverage by $CH_3COO\cdot$ may be involved and may modify the potential profile at the metal–solution interface. It is also found that Q_H is not reduced appreciably from its normal value when acetate ion is present. This supports the absence of specific adsorption of the acetate anion.

(iii) If specific anion adsorption effects were involved, it would be expected, at least at high acetate concentrations, that the oxygen evolution would be partially or completely suppressed also at metals such as Ni, Au, and Fe. However, no Kolbe products have been detected at these metals in aqueous acetate solutions (31, 42, 88) as discussed below. Equally important is the observation that inhibition of the oxygen evolution reaction occurs just as well in acidic (H_2SO_4) solutions of CF_3COOH or acetic acid as in the neutral salt solution of these acids. In the former case, the only anions significantly present are SO_4^{2-} and not the carboxylate anions.

(iv) It has been observed (66) that if the current–potential curve is measured rapidly (applied potential raised at a rate of 16 v sec^{-1}), the rate of the oxygen evolution reaction is *not* decreased and a normal value of the Tafel slope, b, is observed (0.12 v). An interpretation of this observation is that for the oxygen evolution reaction to be inhibited and its Tafel slope to be enhanced to anomalous values, a certain time must elapse, *i.e.*, a minimum quantity of charge (time × current density) must pass per cm^2. The charge passed would most likely result in the formation of an adsorbed intermediate with probably some barrier-layer film behavior which will result in inhibition of oxygen evolution, etc., as will be discussed below. If specific anion adsorption were responsible for inhibition of the oxygen evolution reaction, as Fioshin and Vasil'ev maintain, this effect would still tend to be operative when the electrode potential is changed rapidly since the population of charges in the double layer usually adjusts much more rapidly (than would correspond to 16 v sec^{-1} change in the *applied* potential) to changes of electrode potential.

The role of species produced in the Kolbe reaction in inhibiting the oxygen evolution process is illustrated in another way by the observations of Fioshin and Vasil'ev (67). These authors obtained potentiostatic current–potential curves showing inflection or inversion effects (Tafel slopes negative over a small range of potential) characteristic of deposition of an inhibiting species on the surface. The extent of the inhibition effect depended on the concentration of acetate. Lower concentrations of acetate required higher potentials to be reached before the inhibition inflection arose. The hysteresis between ascending and descending current–potential curves which was observed is characteristic of irreversible inhibition by adsorbed species. The latter species were supposed by Fioshin and Vasil'ev to be acetate ions, but alternative ideas contrary to that view and in favor of discharged radical species have been discussed above. The inhibition effects were also found to be characteristic of the gegen cation of the electrolyte. In their work, the Tafel slope for the lower region (O_2 evolution) was found to be higher than that for the upper region, an effect which, we have suggested elsewhere, is associated with discharged acetate species influencing the Tafel slope for oxygen evolution. The slope for the latter reaction in the absence of acetate is usually lower.

The lower region of the current–potential curve observed by Fioshin and Vasil'ev was regarded as corresponding to oxygen evolution. However, it seems that another process must be involved since the currents passing at the potentials concerned seem to be some 10^5 times too large for oxygen evolution at platinum. Possibly an intermediate parallel reaction to Hofer–Moest and other side products involving the acetate was actually occurring (*cf.* ref 46).

The relative yields of O_2 and CO_2 and C_2H_6 in the acetate Kolbe reaction have been measured by Dickinson and Wynne Jones (42) and are shown in Table V for various anode potentials and current densities using Pt, Ir, Au, and Ni as electrodes. At Ni and Au which form thick oxide films, the Kolbe reaction is virtually completely inhibited (see below).

2. *Relation of the First Hypothesis to Other Problems*

a. Anode Material

It is well known that the Kolbe reaction proceeds inefficiently in *aqueous* medium at electrodes on which the presence of multilayer (phase) oxides is unambiguously established, *e.g.*, in the cases of Ni (42, 88), Au (31, 42, 88), Fe (13), MnO_2 (88), PbO_2 (88, 139). Hence the formation and presence of appreciable oxide may inhibit the adsorption of RCOO· radicals (through metal–oxygen bonds) or R· radicals and hence lead to the absence of adsorbed RCOO· or R· and thus also to normal Tafel slopes. Any enhancement of the oxygen evolution slope to give a line OO (Figure 14) and consequently a crossing-point C would therefore not be possible. In other words, even at the highest potentials, oxygen evolution would be expected still to be the predominant process under such conditions.

In nonaqueous media, however, even on the above electrode materials, oxygen evolution is excluded and the only possible reaction is the one involving "Kolbe" species. In terms of Figure 14, the Tafel regions corresponding to OO and OO′ lines are therefore never involved, and indeed it has been usually observed experimentally that even on electrodes covered by some oxide layer, the Kolbe reaction proceeds with good efficiency in nonaqueous media, *e.g.*, at PbO_2[12] or on oxide–covered Au electrodes in acetate–glacial acetic acid solutions. A consequence of the arguments developed above is that on electrodes covered predominantly by oxides, since R· and RCOO· may not be so easily adsorbed, the Kolbe reaction in nonaqueous media would tend to proceed with initial discharge as the rds; any other step, if rate determining, would imply[13] significant coverage by R· or RCOO·. It has been observed (164) that on gold in nominally anhydrous potassium acetate solution, the Kolbe reaction does in fact proceed on an oxide-covered electrode (the oxide arising from traces of water present) with the initial discharge step as the probable rate-determining stage.

b. Anode Potential

Experimentally, the Kolbe reaction in aqueous solutions usually proceeds with increasing efficiency as the anode potential is raised (*e.g.*, Figure 10). This is easily understood in terms of Figure 14: the higher the anode potential, the greater will be the separation between KK′ and OO′; *i.e.*, the Kolbe reaction will be favored.

c. Concentration of the Electrolyte

It is usually observed that increased concentrations of the electrolyte in aqueous acetate solutions result in an increase of the coulombic efficiency of the Kolbe reaction (Figure 10). Increased bulk concentration $(C_R)_b$ of the reactant component R of the electrolyte would be expected to increase the surface concentration $(C_R)_s$ of the reactant species; the $(C_R)_b$ is related to $(C_R)_s$ by an isotherm of the form

$$(C_R)_s \simeq (C_R)_b \exp\left[-\frac{\Delta\bar{G}_R{}^\circ}{RT}\right]$$

where $\Delta\bar{G}_R{}^\circ$ is the standard electrochemical free energy of adsorption of R and is defined for appropriate standard states for R in the bulk and in the surface layer.

If the Kolbe reaction and the oxygen evolution reaction were proceeding in the same potential region and with comparable rate constants, the increase in coulombic efficiency for ethane formation with increased acetate concentration[14] in aqueous solution would be simply due to increased surface concentration of the reactant species, R. However, when the Tafel line for

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[12] In the case of PbO_2, electrical barrier-layer effects will be relatively unimportant since this substance is a good conductor of electricity, by virtue of its being a degenerate semiconductor, *cf.* its formation and reduction in the lead storage battery.

[13] That is, assuming that equilibria involving $CH_3COO\cdot$ and $CH_3\cdot$ prior to the rate-controlling step are not excessively to the left-hand side of the respective component steps. This restriction does not apply to the earlier arguments given above since appreciable effects on the Q values for oxides are observed under conditions where the Kolbe reaction is proceeding.

[14] This effect of concentration will, of course, only change the rate (at a given overpotential) at concentrations greater than *ca.* 0.5 M where the ψ potential tends to become independent of concentration, so that the effect of the increase of $(C_R)_b$ is no longer cancelled by diminishing ψ (Appendix I) (21, 73, 121). Different effects would, however, arise if the reactant molecule or ion were specifically adsorbed.

the oxygen evolution reaction commences at a lower potential and has a lower slope than the one for the Kolbe reaction, the above explanation for the effect of the concentration of the electrolyte would not be valid. Another explanation which seems plausible is that, at higher bulk acetate concentrations, the surface concentration of the reactant species increases with a consequently increased barrier-layer film effect for the oxygen evolution reaction; this would tend to bring the point C down on the potential axis (see Figure 14), with a consequently more pronounced separation of KK′ and OO′ at higher potentials which would favor the Kolbe reaction.

d. Anomalous Tafel Slopes for the Oxygen Evolution Reaction in Aqueous Acetate Solutions

A matter related to the above considerations is the interpretation of the Tafel slope, observed in the case of oxygen evolution on gold in 1 *M* CH_3COOK solution in water where *no* Kolbe reaction occurs (31, 162). In the acetate solution, some adsorption by $RCOO\cdot$ radicals may still take place giving rise to an effective barrier-layer on the electrode with a consequent increase in the Tafel slopes to 0.09 v (31, 162) from the usual value of 0.045 v (42, 113). This increase in the Tafel slope for the oxygen evolution reaction is perhaps still not high enough to shift OO to OO′ to such an extent that OO′ crosses KK′ (see Figure 14) at some easily accessible potential; since the point C will thus not be easily reached, no Kolbe reaction would be expected. However, if very high concentrations (*e.g.*, $\simeq 10$ *M*) of CH_3COOK were used and if a potentiostat were available which could control the potential of the electrode to values much higher than those usually reached (*ca.* 2.0 v) in this case, the possibility of achieving rates beyond the point C on the line KK′ (see Figure 14) and hence observing the Kolbe reaction would perhaps not be entirely excluded. However, this suggestion has yet to be verified experimentally.

3. Inhibition Inflection

In the potentiostatic steady-state log (i)–V relations for gold in nominally anhydrous 1 *M* CF_3COOK–CF_3COOH solutions, an inhibition inflection is observed in the potential region *ca.* 1.6 to 1.8 v (Figure 11b) (31). This type of inhibition inflection is usually indicative of a coadsorbed inhibiting species; however, this effect is *not* always observed when the presence of a coadsorbed inhibiting species is suggested by other evidence. This inflection behavior would tend to be observed only when both i (*i.e.*, the rate) and Θ (*i.e.*, the coverage) were dependent on potential in the *same* potential region. In such a case, the rate i could be expressed as

$$i = ke^{\alpha VF/RT}e^{-k'VF/RT} = e^{(\alpha - k')VF/RT}$$

where k' is a coefficient expressing the potential dependence of coverage Θ and α is a transfer coefficient determining the potential dependence of the rate in the usual way. When $k' > \alpha$, a reversal of the direction of the log (i)–V line, *i.e.*, an inhibition inflection, will be observed (Figure 11b) as treated previously (4, 85). However, if k is finite but smaller than α, only a *change of slope* in the log (i)–V line would be observed; an inhibition inflection is actually a limiting case of this change of slope, *i.e.*, when the slope changes in sign and the kinetics hence exhibit an inversion with respect to the dependence of rate on potential V, and formally are associated with a negative differential reaction resistance.

Complete reversal effects of the type observed in anodic reactions which proceed at lower potentials (0–1 v E_H), *e.g.*, in the cases of formate and hydrocarbon oxidation, are not usually observed in the Kolbe reaction but some changes of slope of the kind referred to above do arise. The absence of the first effect is understandable when it is noted that initial coverage of the Pt electrode by oxide species has already occurred at potentials up to 1.0–1.2 v E_H, and only secondary changes of the oxide film proceed at potentials higher than the upper limit of this range. Hence the absence of primary inflection effects with change of sign of the Tafel slope is accounted for.

E. RELATION TO HYDROCARBON OXIDATION

It may seem surprising that the Kolbe reaction proceeds well at Pt, one of the most active metals for the electrocatalytic oxidation of hydrocarbons (84, 118). However, the latter process only occurs at quite elevated temperatures, *ca.* 150°, at an active Pt surface when dissociative adsorption of the C–H linkages begins (*e.g.*, deuterium exchange (102) with methane begins to be significant at such temperatures). The fact that $CH_3\cdot$ radicals are most likely to be involved in the Kolbe reaction at room temperature and yet are not appreciably oxidized to CH_3OH or CO_2 implies that it is not necessarily the C–C bond-breaking process that is limiting in the kinetics of oxidation of paraffinic hydrocarbons; facile C–H dissociative adsorption seems also to be a necessary requirement.

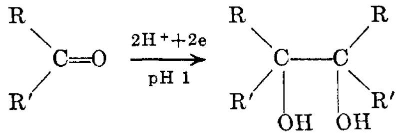
At higher temperatures, however, the Kolbe reaction begins to be suppressed and more extensive oxidation of the R function occurs in a manner more consistent with the observed oxidation of hydrocarbons at even higher temperatures. It thus appears reasonable to presume that the existence of radical coupling to *form* a hydrocarbon R_2 in preference to oxidation of R is only a matter of relative rates of the two processes, in particular with regard to the effects of temperature.

At the platinized platinum surface, where hydrocarbon oxidation is most facile, the Kolbe reaction is usually found not to proceed. However, this is probably because the real current densities required to reach potentials greater than *ca.* 2.2 v in aqueous media are then, practically, unobtainable bearing in mind the normal real:apparent area factor for platinized platinum of 200–400.

VII. OTHER COUPLING REACTIONS

Several other electrochemical coupling reactions are known but have not been studied or used for syntheses by any means as extensively as has the Kolbe reaction. Some well-known or recent examples are summarized below for comparative purposes.

A. REDUCTION OF KETONES TO GIVE PINACOLS



This reaction occurs when R and R′ are either aliphatic or aromatic. Mercury or amalgamated zinc are suitable cathode surfaces. Radical intermediates have been suggested.

B. REDUCTION OF ACRYLONITRILE TO ADIPONITRILE

A number of electrohydrodimerization reactions occur with activated olefinic substrates, as studied by Baizer in a series of papers (63). An important example is

$$2CH_2{=}CHCN \xrightarrow{2H^+ + 2e} CN(CH_2)_4CN$$

which proceeds by a carbanion intermediate at mercury cathodes and is used as a commercial process. Analogous reactions with other substrates can be achieved by electrolysis of cyanoalkylphosphonium compounds (63).

C. REDUCTION OF N-ALKYLPYRIDINIUM IONS AND OTHER CATIONS

The cathodic coupling reaction (154)

is known. A related reaction with symmetrical aliphatic tetraalkylammonium salts to give a dimer of the alkyl function does not, however, occur significantly at Pt or Hg in anhydrous acetonitrile, but the corresponding reaction with more complex quaternary ammonium salts, *e.g.*, triethylbenzylammonium, does proceed (63) to give the expected dimer, bibenzyl.

D. ELECTROLYSIS OF BORONIC ACIDS (177)

This recently investigated reaction (177) yields hydrocarbons but not the expected coupled product. With *n*-butylboronic acid, butenes and *n*-butane are formed but no octane (*cf.* the products of the Kolbe reaction with propionates).

E. ELECTROLYSIS OF SOLUTIONS CONTAINING TROPYLIUM IONS

In acid solutions, reduction of the tropyl cation has been shown (176) to lead to bitropyl. Adsorption of a tropyl radical is regarded as being involved.

VIII. CONCLUSIONS

In conclusion, it may generally be stated that the reaction pathway and rate-determining stage in the over-all Kolbe reaction is still a matter of dispute among many investigators. This is partly the result of the situation that, as in other electrochemical processes, mechanisms must be considered individually for (a) the electrode metal concerned, (b) the type of solution and solvent used, and (c) the type of reactant carboxylate salt involved. A universal general mechanism cannot be anticipated. However, a number of definite conclusions that may be made about the Kolbe reaction and the various methods by which it has been studied are as follows.

(i) High Tafel slopes and high degrees of coverage of the electrode have been consistently observed by various authors; the experimental evidence suggests either the involvement of a dipole barrier-layer of adsorbed Kolbe species on the electrode or substantial kinetic effects of adsorbed reactant anions and, in aqueous media, surface oxide.

(ii) The pulse studies aimed at determining the order of reaction give, at the moment, somewhat inconsistent results.

(iii) The pulse studies of the type conducted by Lippincott and Wilson and by Fleischmann, Mansfield, and Wynne-Jones seem to be a promising approach, and further work of this type is required; hitherto, however, this method has not yielded very clear-cut results; also some difficulties of a conceptual nature arise in the interpretation of the results reported.

(iv) The presence of surface oxides may be demonstrated in aqueous media and must be coadsorbed with any "Kolbe" adsorbed species such as $RCOO\cdot$ or $R\cdot$; the surface oxides, it has been concluded, usually play an inhibitory role and may be involved in the production of side products. Surface oxides are not required for the reaction to proceed and the Kolbe reaction is generally more efficient in nonaqueous media.

(v) The presence of $RCOO\cdot$ and/or $R\cdot$ free radicals on the electrode surface has been strongly indicated in several studies.

(vi) Some mechanisms can be fairly unambiguously excluded from further consideration. In a number of related cases, definite mechanisms can be proposed which are supported by reasonably consistent experimental evidence and critical kinetic criteria.

(vii) The reason for failure of the Kolbe reaction to occur under certain conditions seem to be at least qualitatively understood.

(viii) Reasons for inhibition of the oxygen evolution reaction, and the resulting preferred evolution of Kolbe products at the noble metals, can now be proposed on the basis of general principles of electrode kinetics.

(ix) Side products may arise variously through (a) formation of carbonium ions, with formation of characteristic rearrangement products, (b) by reaction between adsorbed radicals such as R· and RCOO·, or between such radicals and the solvent, and (c) by reaction of such radicals with the surface oxide formed at the noble metals in aqueous media. Mechanism a may be preferred with carboxylate structures having centers of relatively low ionization potential.

(x) Chemisorption effects cannot be neglected in considering any possible mechanisms, and the role of such effects and surface catalyzed reaction steps between adsorbed free radicals must be borne in mind, particularly when the course of the Kolbe reaction at the noble metals is under examination.

(xi) Cleaner and more simple reactions seem to proceed in nonaqueous media, presumably because electrode surface oxides, which are formed anodically in aqueous media above potentials of *ca.* 0.8–1.0 v E_H, are not involved.

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IX. Appendix I. Kinetic Equations

It is anticipated that this review will be read not only by specialists in electrochemistry but also by those interested in organic chemistry and organic reaction mechanisms. Accordingly, for the convenience of such readers, we have considered it desirable to include here and in Appendix II some brief and simplified reference to the origin of potential-dependent rates in the kinetics of electrode reactions (5, 21, 107) and some remarks on capacitance and coverage of electrode surfaces by adsorbed electroactive species (21, 27, 52, 74, 79, 157). These matters have, however, been treated in much more detail in texts of electrochemistry (21) and in well-known original papers.

Basically the rate of an electrode reaction is determined, as in nonelectrochemical heterogeneous reactions, by a rate constant $\bar{k}$ calculated on a cm^{-2} basis of surface area, and by surface coverage, Θ, of reactants or by the free surface available, $1 - \Theta$. However, the rate constant $\bar{k}$ in *electro*chemical rate processes is dependent on potential as shown below. For a z-electron oxidation, the rate v (cm^{-2}) is related to the current density by

$$i = zFv$$

and v is determined, at a given reactant concentration $(C_R)_s$ at the surface by

$$v = \bar{k}_1(C_R)_s(1 - \Theta)$$

for a discharge step such as

$$X^- + M \xrightarrow{\bar{k}_1} X/M + e \qquad \text{(Eq A1)}$$

involving, for example, one electron and requiring one site on the metal M for adsorption of the product X arising from a reactant R (R = X$^-$). In an electrochemical reaction, the rate constant $\bar{k}_1$ is related to a standard free energy of activation $\Delta\bar{G}^{\circ\ddagger}$ as in other types of reactions except that it is useful to distinguish the "electrochemical" free energy of activation $\Delta\bar{G}^{\circ\ddagger}$ from its "chemical" component $\Delta G^{\circ\ddagger}$ where (for a one-electron discharge event)

$$\Delta\bar{G}^{\circ\ddagger} = \Delta G^{\circ\ddagger} - \beta F(V - \psi)$$

V is the total metal–solution potential difference (pd) at the single interface (and is therefore not a measurable quantity), and ψ is that part of V which falls between the reactant adsorbed layer and the bulk of the solution due to double-layer ion distribution effects; the free energy of activation is thus controlled by the electrode potential to an extent determined by the quantity β. β is a symmetry factor, often near 0.5, analogous to Brønsted's α coefficient in the treatment of acid–base proton-transfer kinetics and equilibria, and can be regarded either as being determined by the relative slopes of potential energy curves for reactants and products at the "crossing region" or as measuring the average charge on the activated complex in the charge-transfer step. Since $\bar{k}_1$ will be defined in the usual way (*cf.* the theory of absolute reaction rates) as

$$\bar{k}_1 = \frac{kT}{h}\exp[\Delta\bar{G}^{\circ\ddagger}/RT]$$

it follows that v will be an exponential function of the metal–solution pd. The potential V can be related to a measured emf of a cell passing current when the potential of the working electrode is referred to that (constant value) of some standard reversible reference electrode in the same solution, at which the single electrode solution pd is V_r; then $E = V - V_r$ so that V is then a function of a measurable pd E. It then follows obviously that log v and hence log i is a linear function of E with a slope of $2.3RT/\beta F$ known as Tafel's constant b. It is worth noting here, since in many studies of the Kolbe reaction this matter has not received attention, that the pd E which determines the rate is by no means identical with the applied voltage $\Delta V_{a,c}$ between the anode a and the cathode c. In many reports of work on the Kolbe reaction, $\Delta V_{a,c}$ has been specified while it is really only E referred to a third (reference) electrode at which no current is passing that has any electrochemical significance in the characterization and determination of the rate v or current density i; the current *density* rather than the current must also be the specified rate quantity.

In a number of reactions, a step involving the desorptive removal of adsorbed X (X/M in Eq A1) such as

$$\mathrm{X/M} + \mathrm{Y}^- \xrightarrow{\bar{k}_2} \mathrm{XY} + e \qquad \text{(Eq A2)}$$

is involved and will have a rate given by

$$v_{xy} = \bar{k}_2(C_{y^-})_s\Theta_x$$

If Eq A2 is the rate-controlling step relative to Eq A1, the latter process may be regarded as at quasi-equilibrium and Θ_x is then a function of potential having the form

$$\frac{\Theta_x}{1 - \Theta_x} = K_1 \exp(VF/RT)$$

under Langmuir conditions of adsorption of X. At low Θ_x $(1 - \Theta_x \rightarrow 1)$ and for $\bar{k}_2$ having the same form as $\bar{k}_1$, v_{xy} becomes potential independent both on account of the potential dependence of Θ_x and of $\bar{k}_2$; the resultant potential dependence is $\exp(\beta VF/RT)\exp(VF/RT)$ so that log v is now dependent on V with a Tafel coefficient $2.3RT/(1 + \beta)F$. It will be seen that this type of case always gives rise to Tafel coefficients *less* than $2.3RT/\beta F$. In the above, it has been assumed that $\bar{k}_2$ depends on V through a β factor similar to that involved in $\bar{k}_1$. In some of the special cases considered in the text, the effective fraction of $V - \psi$ available for ion discharge is diminished by a further fraction α owing to the presence of an oriented adsorbed layer of dipolar adsorbed species, so that the *effective* value of β for ion discharge processes can then be appreciably less than 0.5, whence anomalously high values of Tafel's coefficient can arise.

X. APPENDIX II. CAPACITANCE AND ADSORBED INTERMEDIATES

In a number of places in the text, reference has been made to the capacitance C associated with adsorbed intermediates and the potential, $V_{C_{\max}}$, associated with the maximum capacity. Here we show briefly the origin and significance of these quantities.

If an electroactive intermediate X is formed in an adsorbed state X/M at the electrode surface and the process (see Appendix I)

$$\mathrm{X}^- + \mathrm{M} \rightleftharpoons \mathrm{X/M} + e \qquad \text{(Eq A3)}$$

is relatively reversible, X/M can be referred to as an electroactive adsorbed intermediate since it can be removed by the reverse direction of Eq A3 in a reductive (cathodic) transient. By equating the forward and backward rates of the processes comprising Eq A3, the relation given previously, *viz.*

$$\frac{\Theta_x}{1 - \Theta_x} = K_1 \exp(VF/RT)$$

is easily obtained for a metal–solution pd of V. It is also to be noted that in depositing X to an extent of fractional coverage Θ, a charge Q_x, equal to $k'\Theta$ is required where k' is a measure of the number of electrons required per cm^2 to produce full coverage of the surface. For H chemisorption at Pt, $k' \cong 200$ μcoulombs cm^2; for $\mathrm{CH_3COO\cdot}$ adsorption, k' is correspondingly less because of the larger area occupied by this radical. The relation for Θ_x indicates that Θ_x increases with increasing potential so that the corresponding charge Q_x, *viz.* $k'\Theta_x$, required to produce a given coverage Θ_x, is a function of potential. The derivative dQ_x/dV has therefore the form of a differential electrical capacitance C_x associated with the potential dependence of adsorption of the electroactive intermediates considered. Differentiation of Θ_x with regard to V then gives

$$C_x = \frac{k'FK_1 \exp(VF/RT)}{RT[1 + K_1 \exp(VF/RT)]^2}$$

or in terms of Θ_x

$$C_x = \frac{k'F}{RT}\Theta_x(1 - \Theta_x)$$

which indicates that C_x has a maximum value at $\Theta_x = {}^1/_2$ from which the corresponding relative potential of the maximum in C_x can be obtained, *i.e.*, the potential we have referred to above as $V_{C_{\max}}$. The relation for Θ_x is of course an idealized one, but other treatments have been given for cases when (a) the surface is heterogeneous and Langmuir's isotherm does not apply, and (b) when a degree of nonequilibrium obtains in reaction A3 (27, 52, 74, 79, 157).

Observation of the potential of the maximum capacitance is a useful factor for characterization of the adsorbed species involved, since the potential required to reach half-coverage is determined by K_1 and hence the standard free energy of adsorption of the species. When interaction and heterogeneity effects are involved, the potential for half-coverage depends additionally on these factors, which then lead to an apparent variation of K_1 with coverage and an increase of the range of potentials over which Θ_x increases from small values to near unity.

The course of a typical reductive transient and its differential coefficient (to which C is related) is shown in Figure 15.

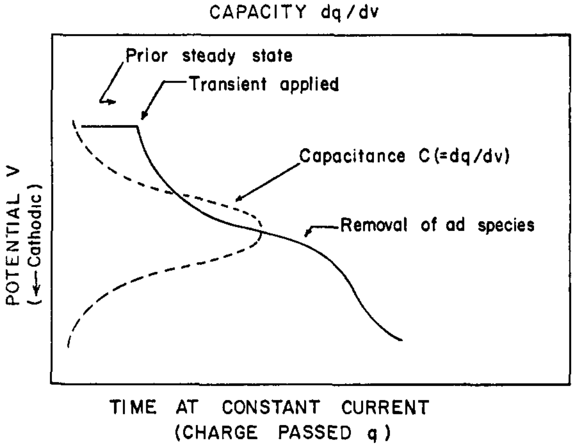

Figure 15.—Schematic discharging curve (solid line) for cathodic removal of reducible adsorbed species at an electrode by application of a constant current pulse. Dashed line shows differential coefficient as a function of time in the pulse; this differential is equivalent to a capacitance associated with the removal of the electroactive adsorbed species (27, 28, 108).

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