Kolbe Electrosynthesis. Role of CO-Adsorbed Surface Oxides

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The classical work of Kolbe[1] in 1849 constituted the first detailed study of anodic reactions of the form below

$$2RCOO^- \longrightarrow R_2 + 2CO_2 + 2e \qquad (I)$$

giving R_2 from a carboxylate $RCOO^-$, where R is an alkyl or substituted alkyl residue. This reaction has since been the subject of many investigations particularly with regard to synthetic applications (for reviews, see ref 2–5).

Most previous work on the Kolbe synthesis, and the associated Hofer–Moest reaction, has been carried out in aqueous or water-containing media, usually at the platinum electrode. Recently[6,7] and earlier,[8] it has become recognized that the Pt electrode in aqueous solutions of alkalis, inorganic oxyanion acids, or their salts becomes oxidized at its surface with a very thin layer of surface oxide or adsorbed O-containing species at potentials more anodic than about 1.0 v on the reversible hydrogen electrode scale for the same solution. However, it does not seem to have been generally recognized that the Kolbe reaction and any side processes may therefore also be proceeding on an oxide-covered surface of Pt rather than on that of the bare metal and that this surface oxide may hence be involved directly in some of the side reactions. In this Note we briefly report evidence indicating the presence and kinetic role of surface oxide at Pt and Au when reaction I is taking place in aqueous and water-containing "nonaqueous" media. Some results of electrochemical studies are presented in so far as these observations may be of interest and importance in considering the consecutive steps[5] and side reactions associated with reaction I. The existence of surface oxides on Pt anodes in carboxylate salt solutions was first indicated in some previous work,[5,9] but systematic investigations on the presence and role of the oxide as a function of the water content of the solvent have not been reported. It may be noted that in discussing mechanisms of the Kolbe reaction in aqueous and nonaqueous solutions, it is of considerable importance to establish the surface coverage and, if possible, the identity of adsorbed species such as oxide, acyloxy, and alkyl radicals. Also the anode potential measured against some reference electrode, and the current *density*, must be specified; the often-quoted over-all voltage applied to the cell, is electrochemically meaningless.

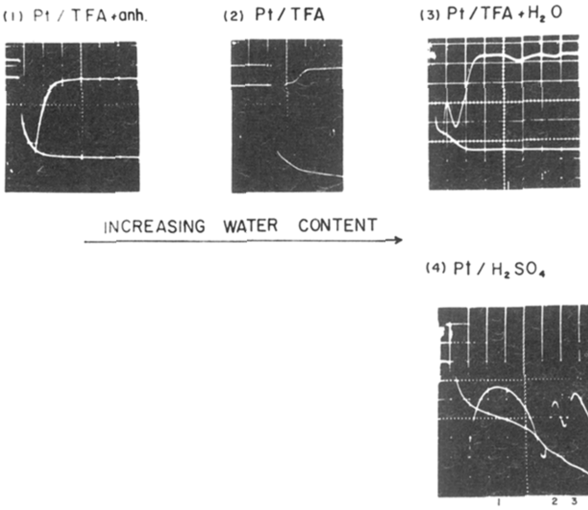

Figure 1.—Constant current transients (5°) (together with the corresponding differentiated profiles) showing, qualitatively, cathodic reduction behavior of anodically formed adsorbed intermediates (peak 1), under the indicated conditions; peaks 2 and 3 are for hydrogen atom production. The cases and charges (Q) (Mc cm^{-2}), respectively, are (1) Pt–TFA + anhydride, no peak (0); (2) Pt–TFA, peak 1 (0.15); (3) Pt–TFA + H_2O, peak 1, (0.71); peaks 2 and 3 (1.87); (4) Pt–H_2SO_4, peak 1 (1.3), peaks 2 and 3 (0.7). Charge Q = constant reduction current × time of arrest, *i.e.*, $\Delta t i_-$.

The kinetics of reaction I have been studied on Pt and Au in *very* anhydrous, *nominally* anhydrous (*i.e.*, solutions containing traces of water), and *aqueous* solutions of 1 *M* potassium trifluoroacetate (KTFA) in trifluoroacetic acid (TFA). This system gives[5] good anodic yields of C_2F_6 and was chosen to minimize side reactions involving H abstraction which can occur when R = CH_3. The cell design, solution, electrode preparation, and gas purification, etc, were as described previously.[5] In the present work, potentiostatic[10] steady-state and potentiodynamic[6,7,10] nonsteady-state electrochemical measurements were made which yield information on the kinetic behavior of the over-all Kolbe reaction. Rapid (0.1–10 msec) galvanostatic[10] cathodic discharge experiments (*cf.* ref 5) gave information on the extent of coverage of the anode by electroactive (*i.e.*, cathodically reducible) adsorbed intermediates formed in the prior steady state. The basic principles of these approaches have been discussed previously[10] and experimental electrochemical procedures will be described in detail elsewhere.[11]

Potential − log [rate] relations for the Kolbe reaction on Pt in *very* anhydrous 1 *M* KTFA–TFA solutions prepared by addition of <1% of trifluoroacetic anhydride to the chemically dried solvent (boric anhydride, anhydrous $CuSO_4$), nominally anhydrous 1 *M* KTFA–TFA solutions and aqueous 1 *M* KTFA–TFA were compared. At a *given* potential,[12] the rate, measured by the anodic current density i_+, is the highest in the very anhydrous solution and lowest in the aqueous

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(1) H. Kolbe, *Ann. Chem.*, **69**, 257 (1849).

(2) S. Glasstone and A. Hickling, *J. Chem. Soc.*, 1878 (1934); 820 (1936).

(3) B. C. L. Weedon, *Quart. Rev.* (London), **6**, 380 (1952).

(4) M. J. Allen, "Organic Electrode Processes," Reinhold Publishing Corp., New York, N. Y., 1958.

(5) B. E. Conway and M. Dzieciuch, *Can. J. Chem.*, **41**, 21, 38, 55 (1963); A. Vijh and B. E. Conway, *Chem. Rev.*, in press.

(6) M. Breiter, C. A. Knorr, and W. Volkl, *Z. Elektrochem.*, **59**, 881 (1955); M. Breiter, K. Francke, and C. A. Knorr, *ibid.*, **63**, 226 (1959).

(7) F. G. Will and C. A. Knorr, *Z. Elektrochem.*, **64**, 258 (1960).

(8) J. D. Pearson and J. A. V. Butler, *Trans. Faraday Soc.*, **34**, 1163 (1938).

(9) T. Dickinson and W. F. K. Wynne-Jones, *ibid.*, **58**, 382, 388, 400 (1962); see also J. R. Mansfield, M. Fleischmann, and W. F. K. Wynne-Jones, *J. Electroanal. Chem.*, **10**, 511; 522 (1965).

(10) For example, see B. E. Conway, "Theory and Principles of Electrode Processes," Ronald Press, New York, N. Y., 1965.

(11) B. E. Conway and A. K. Vijh, *Ber. Bunsenges.*, in press.

(12) It may be shown[11] 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 the nonaqueous medium so that comparisons of rates at the same measured potentials are legitimate.

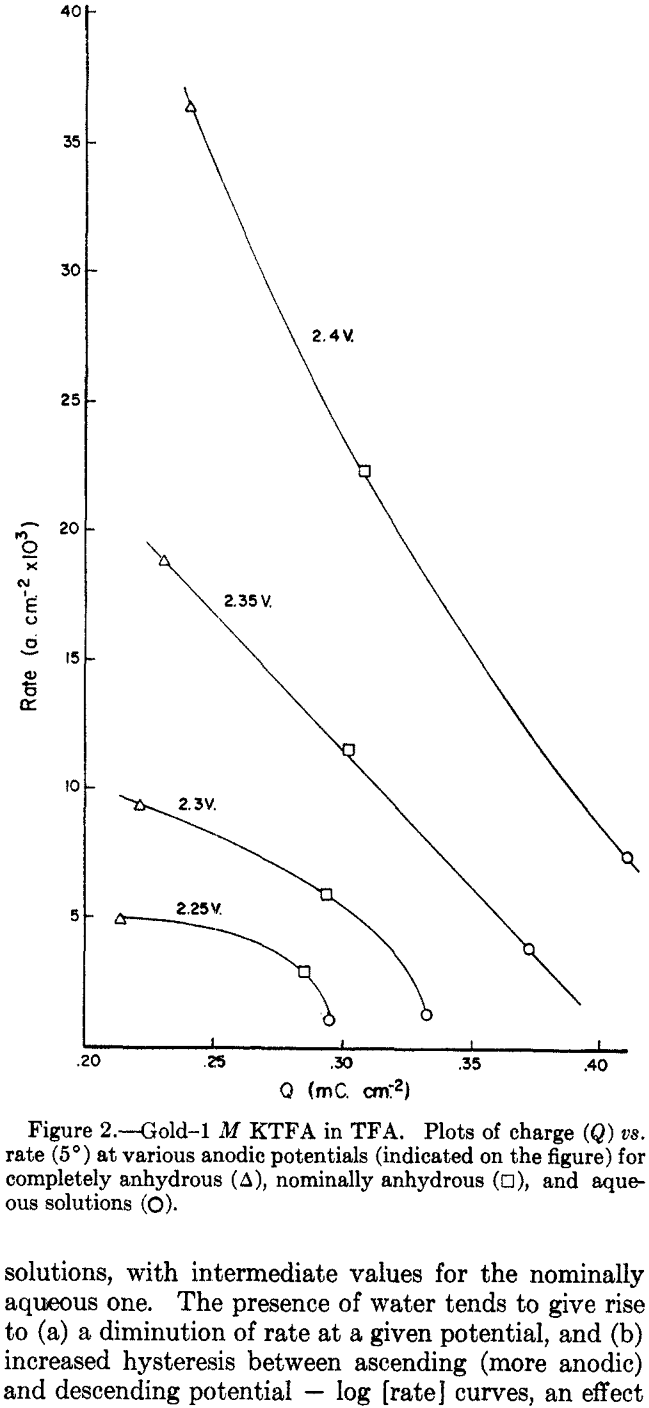

Figure 2.—Gold-1 *M* KTFA in TFA. Plots of charge (*Q*) *vs.* rate (5°) at various anodic potentials (indicated on the figure) for completely anhydrous (Δ), nominally anhydrous (□), and aqueous solutions (O).

solutions, with intermediate values for the nominally aqueous one. The presence of water tends to give rise to (a) a diminution of rate at a given potential, and (b) increased hysteresis between ascending (more anodic) and descending potential − log [rate] curves, an effect which is known in other electrochemical reactions to be characteristic of the formation and irreversible removal of surface oxide films derived from H_2O. In the completely anhydrous solution, virtually no such hysteresis is observed throughout the potential − log [*i*] curve.

The surface oxide on Pt, if present, may also be detected[8,10] more directly by constant current cathodic reduction over a time interval of 0.1–10 msec. That the reduction was of a *surface* species was shown by demonstrating that the transition time for the reduction was inversely proportional to the cathodic current density.[10]

In Figure 1, four oscilloscope photographs are shown; three of these represent the electrochemical reduction behavior of the intermediates adsorbed on the electrode surface. The curves, and their differentiated profiles, represent the course of the time dependence of the potential of the electrode at which the Kolbe reaction was previously taking place, during reduction at a constant cathodic current density i_- from anodic potentials previously maintained constant by a potentiostat. The profiles in Figure 1 (1–3) are for the three types of trifluoroacetate solution studied; the fourth photograph [Figure 1 (4)] shows, for comparison, the transient for the adsorbed species (which can only be 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[5,10] the presence of adsorbed intermediates, and the charge required for their reductive removal is given by $\Delta t i_-$. 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 adsorbed oxide originating from the traces of water present in this solution through the reaction $\text{Pt} + H_2O \rightarrow \text{“PtOH”} + H^+ + e$ or $\text{Pt} + H_2O \rightarrow \text{“PtO”} + 2H^+ + 2e$. There is a large arrest under aqueous solution conditions, indicating appreciable coverage by adsorbed species, *e.g.*, oxide arising from the water in the aqueous medium. That these species may be identified with surface oxide is indicated among other more indirect evidence,[11] by the fact that the potential range over which the reduction occurs is almost identical with that over which the corresponding reduction occurs in aqueous H_2SO_4 or $HClO_4$ media where only oxide can be present on the surface.

From the foregoing discussion, the following may be concluded. An increase of water concentration 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 water is the likely source of the electrochemically adsorbed species which diminish the rate of reaction I, which like all electrode reactions is a process occurring heterogeneously at the metal interface.

The foregoing conclusion also holds for the case of reaction I proceeding on gold in the three types of solution studied. In Figure 2, a family of plots is presented and each of these relations refers to a given value of electrode potential in 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 to results obtained for the respective 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 charge *Q* for the cathodic reduction of species on the surface increases but the electrochemical rate correspondingly decreases. This, again, indicates that increasing amounts of adsorbed species, presumably the surface oxide, arise from increasing amounts of water present in the solution; the presence of this surface or adsorbed "oxide" results in a corresponding decrease in reaction rate. However, it is to be noted that, quantitatively, the charge associated with oxide coverage in the Kolbe reaction both with KTFA and potassium acetate in aqueous acetic acid,[11] is substantially lower than that observable when the electrode is anodically polarized in aqueous sulfuric acid alone.

In conclusion, it may be stated that the presence of water in the solution is not only not necessary for the Kolbe reaction to proceed[9] but in fact leads to significant inhibition effects. This is also borne out by yield studies[4,5] where the best yields of R_2 (96% in the case[5] of KTFA giving C_2F_6) are usually obtained in a nonaqueous medium, *e.g.*, the anhydrous acid itself containing its own salt as electrolyte.

The above observations may also have a bearing on conclusions which have been made regarding the possible role of carbonium ions[13] in the Kolbe reaction as deduced from the nature of side products. Thus, products such as alcohols ROH or esters which can be formed,[3] might arise, it seems, just as well from steps involving heterogeneous oxidation of adsorbed $R\cdot$ radicals by the Pt surface oxide as from anodic ionisation to form R^+ and subsequent rapid reaction with the solvent or electrolyte anions. The entity $R\cdot$, of course, can arise from decarboxylation of $RCOO\cdot$[14] produced by discharge of the carboxylate ion.[5]

Acknowledgment.—Grateful acknowledgment is made to the National Research Council, Canada, for support of this work. One of us (A. K. V.) acknowledges the award of a Fellowship from the Sprague Electric Co.

[13] E. J. Corey, N. L. Bauld, R. T. Lalonde, J. Casanova, Jr., and E. T. Kaiser, *J. Am. Chem. Soc.*, **82**, 2645 (1960).

[14] A. Crum-Brown and J. Walker, *Ann.*, **261**, 107 (1891).

Novel Rearrangement Products of 2,2-Dimethyl-1-(tetrahydro-2-furyl)-1,3-propanediol

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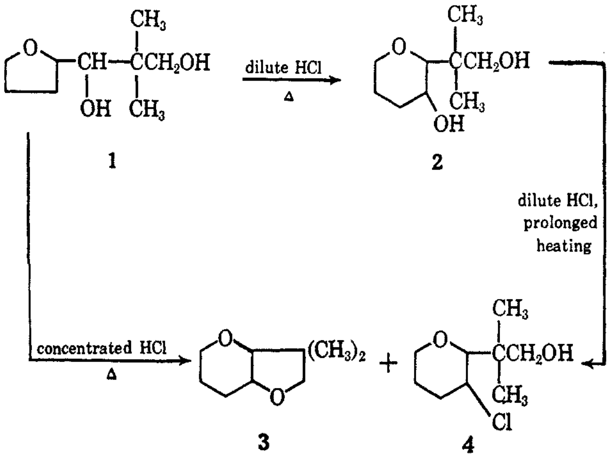
We have found that the furan ring of 2,2-dimethyl-1-(tetrahydro-2-furyl)-1,3-propanediol (**1**) enlarges in the presence of aqueous hydrochloric acid to form three tetrahydropyran derivatives, **2–4**. The relative amount of each compound formed depends upon the acid concentration and the reaction time. (See Scheme I.) This ring enlargement is similar to the isomerization of tetrahydrofurfuryl alcohol to 2,3-dihydropyran.[1]

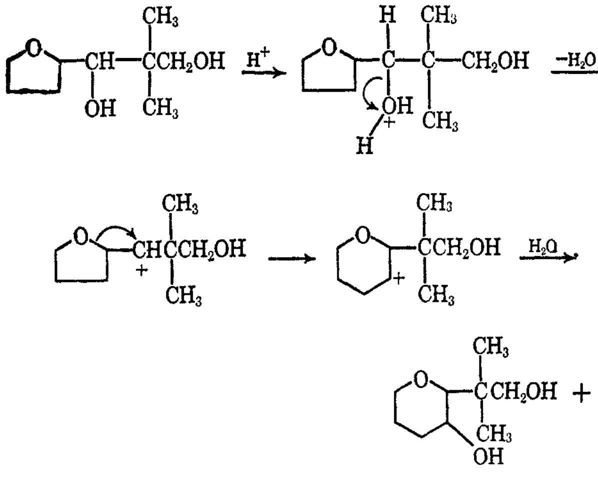
When dilute hydrochloric acid was used, tetrahydro-3-hydroxy-β,β-dimethylpyran-2-ethanol (**2**) was the major product. Concentrated hydrochloric acid or prolonged heating in dilute acid was necessary to form 3-chlorotetrahydro-β,β-dimethylpyran-2-ethanol (**4**) and hexahydro-3,3-dimethylfuro[3,2-*b*]pyran (**3**). When either *p*-toluenesulfonic acid or sulfuric acid was used, the product was mostly hexahydro-3,3-dimethylfuro[3,2-*b*]pyran (**3**). Vapor phase chromatography was used to follow one reaction in which dilute hydrochloric acid was used. Although **2** formed first, it gradually was converted to **3** and **4** on prolonged heating.

SCHEME I



A possible mechanism for this rearrangement is shown in Scheme II below in which the secondary OH group is protonated and water is eliminated to form a carbonium ion.

SCHEME II



Each compound reported except hexahydro-3,3-dimethylfuro[3,2-*b*]pyran (**3**) is a mixture of geometric isomers. No attempt was made to separate each isomer. The structure of each compound was assigned on the basis of nmr data in conjunction with infrared and elemental analyses.

Experimental Section

2,2-Dimethyl-1-(tetrahydro-2-furyl)-1,3-propanediol (1).[2]—A mixture of 2-furaldehyde (96 g, 1 mole) and isobutyraldehyde (144 g, 2 moles) was slowly added with stirring to aqueous 1% sodium hydroxide; the reaction temperature was kept at 10–15°. After the addition of the aldehydes was complete, the mixture was stirred for 1 hr. The heavy oil which separated was extracted with ethyl ether, and the ethereal solution was washed thoroughly with water to remove the sodium hydroxide. Evapo-

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[1] R. L. Sawyer and D. W. Andrus, "Organic Syntheses," Coll. Vol. III, E. C. Horning, Ed., John Wiley and Sons, Inc., New York, N. Y., 1955, pp 276, 277.

[2] The aldol condensation of benzaldehyde with isobutyraldehyde has been described by E. Späth, R. Lorenz, and E. Altman, *Ber.*, **76B**, 513 (1943).