Tetrahedron Vol. 47, No. 4/5, pp. 809-829, 1991
Printed in Great Britain

0040-4020/91 $3.00+.00
© 1991 Pergamon Press plc

A PRACTICAL SYSTEM FOR MANGANESE(III)-MEDIATED ELECTROCHEMICAL SYNTHESIS OF SORBIC ACID PRECURSORS

J. P. Coleman, R. C. Hallcher, D. E. McMackins, T. E. Rogers and J. H. Wagenknecht
Monsanto Company, 800 N. Lindbergh Blvd., St. Louis, MO 63167, U.S.A.

(*Received in USA* 17 *August* 1990)

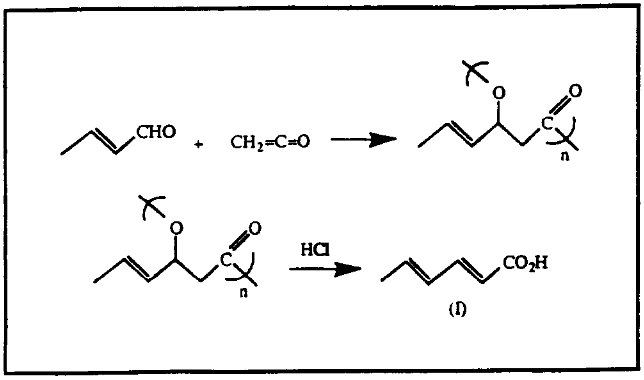
Abstract: An efficient, practical, electrochemical system was developed for the synthesis of a mixture of 4-acetoxy-5-hexenoic acid and *trans*-6-acetoxy-4-hexenoic acid *via* manganese(III)-mediated oxidation of acetic acid-acetic anhydride in the presence of butadiene. Copper(II) co-catalyst enhanced the efficiency of this oxidation and copper(I) was shown to catalyze *in situ* conversion of the acetoxyhexenoic acids into γ-vinyl-γ-butyrolactone.

INTRODUCTION

Sorbic acid(I) is a food preservative produced on a large commercial scale and of demonstrated efficacy, particularly against molds.[1]

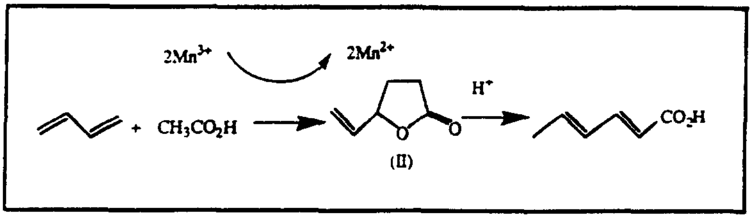
(I)

Monsanto commercialized a process for sorbic acid utilizing the combination of ketene and crotonaldehyde to give a polyester which was subsequently hydrolyzed to sorbic acid[2] (Scheme 1).



Scheme 1

Some early difficulties led to a screening of other potential commercial routes to (I) and, of a large number of other routes studied, the most attractive appeared to be based on the manganese (III)-mediated oxidative coupling of butadiene and acetic acid to give γ-vinyl-γ-butyrolactone(II) which may be further converted into sorbic acid (Scheme 2) under acid catalysis.[3, 4]



Scheme 2

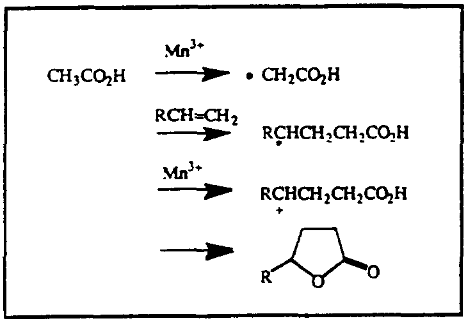
As previously reported this was not a commercially viable reaction sequence, inasmuch as the use of stoichiometric manganese(III) was required. Our aim was to develop this reaction as an electrochemical oxidation, using only catalytic amounts of manganese salts (by continuously reoxidizing the manganese(II) formed in the reaction to manganese(III)), and our studies in pursuit of this aim are reported here.

The *oxidation of manganese(II) to manganese(III), either chemically*[5] *or electro*chemically[6], has been reported previously. However, the success of our work required a regeneration process for manganese(III) which could sustain a commercially attractive level of productivity in the medium of immediate interest, namely acetic acid. We, therefore, undertook a study of this reaction in isolation, as well as in combination with the chemical reaction described above.

Electrochemically-driven reactions of this type have previously been reported for chromium[7] and for cerium[8].

The chemical literature is rich with examples of syntheses involving the use of manganese(III) as an oxidant and references to many of these may be found in recent publications by Snider[9] and Fristad[10].

Bush and Finkbeiner[11], and Heiba[12] studied the reaction between various olefins and manganic acetate in acetic acid. The products were γ-lactones thought to be formed by the addition of a carboxymethyl radical to the olefin, followed by oxidation to the carbonium ion and subsequent cyclization (Scheme 3).



Scheme 3

Hessel[5] and deKlein[13] showed that the decomposition of manganic acetate is accelerated by acetic anhydride, the corresponding radical being assumed to be more stable.

Saturated carboxylic acids were obtained in a free radical chain reaction from olefins and manganese(III) in acetic acid-anhydride.[14] More recently, the electrochemically-mediated carboxymethylation of styrene derivatives was reported by Nishiguchi *et. al.*[15]

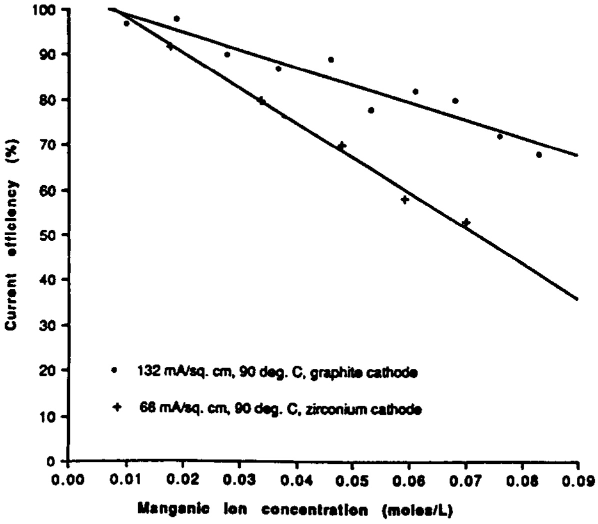
Another study by Kochi had made the interesting observation[16] that, in the manganese(III) mediated oxidation of carboxylates, copper(II) oxidizes intermediate free radical species to carbonium ions far more efficiently than does manganese(III), in spite of its lower oxidation potential. We were able to use this observation to significant advantage in our studies.

RESULTS AND DISCUSSION

Manganese(III) Generation

Early studies on the simple system acetic acid-potassium acetate [2.38 *M*]-manganese(II) acetate tetrahydrate [0.17 *mM*], in an undivided flow cell, confirmed that manganese(III) may be generated at realistic rates in a commercially viable cell [6 (d)]. Using graphite electrodes it was found that at 100°C manganese(III) was formed with current efficiencies greater than 80%, at current densities up to 130 mA/cm^2 with a flow rate from 0.22 m/s to 2.2 m/s across the electrodes. Figure (I) shows a plot of incremental current efficiency *vs* manganese(III) concentration.

Figure I: Steady State Current Efficiency vs. Manganic Ion Concentration: Undivided Cell



A number of observations were made in relation to loss of current efficiency. At higher current density (200 mA/cm^2), significant amounts of methane, ethane and carbon dioxide, absent at lower current density, were detected, confirming a high potential excursion into the regime of the Kolbe reaction when manganese(II) concentration can no longer support the impressed current. A similar effect was observed by decreasing manganese(II) concentration (0.08 *M*) at 100 mA/cm^2.

Decreasing supporting electrolyte concentration from 1.28 *M* to 0.128 *M* caused almost a 50% drop in current efficiency and a five-fold voltage increase across the cell. Under conditions of low supporting electrolyte concentration manganese species are forced to carry a more significant portion of the current through the solution and thus back-reduction of manganese(III) becomes a more efficient process in an undivided cell.

Addition of acetic anhydride, sufficient to react with the water present, caused no significant change in the results obtained.

Thus it seemed, at least in the absence of complications arising from any subsequent chemistry, that a practical process for *in situ* regeneration of manganese(III) appeared possible.

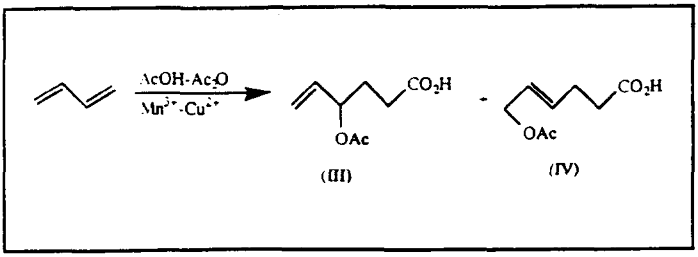
Reactions With *In-Situ* Manganese(III) Generation

A. Batch Cells

As a starting point we repeated the reaction of butadiene and acetic acid [3], using stoichiometric manganese(III), and obtained yields of lactone (II) in the 30-40% range.

Our first electrochemical experiments were then carried out using acetic acid-sodium acetate-manganese(II) acetate-butadiene in a glass Fisher-Porter bottle, containing two 1/4 inch diameter graphite rod electrodes, at 110°C/50 psig. A modest current efficiency of 19% was observed for lactone(II) formation.

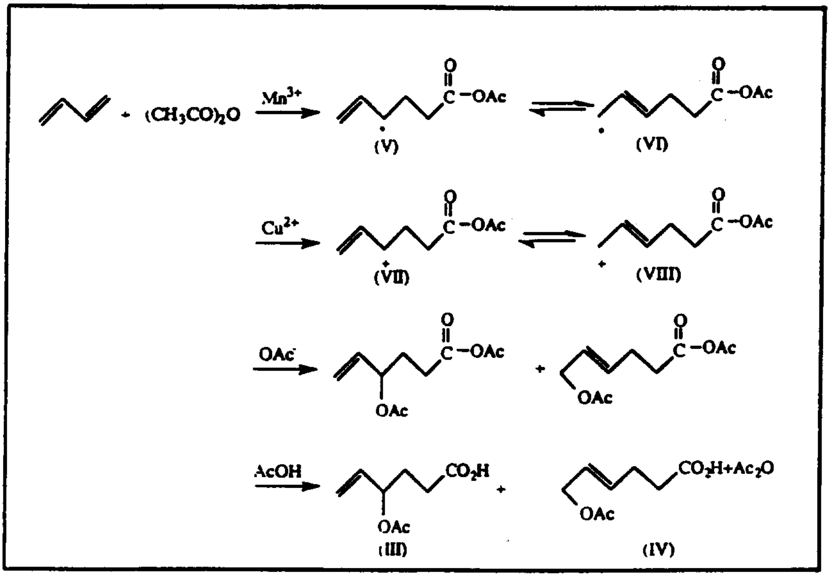
Addition of acetic anhydride and copper(II) acetate to this simple reaction system simultaneously improved the current efficiency to a more respectable 51% and modified the reaction product, forming the mixture of acetoxyhexenoic acids (III) and (IV) instead of the lactone (Scheme 4).



Scheme 4

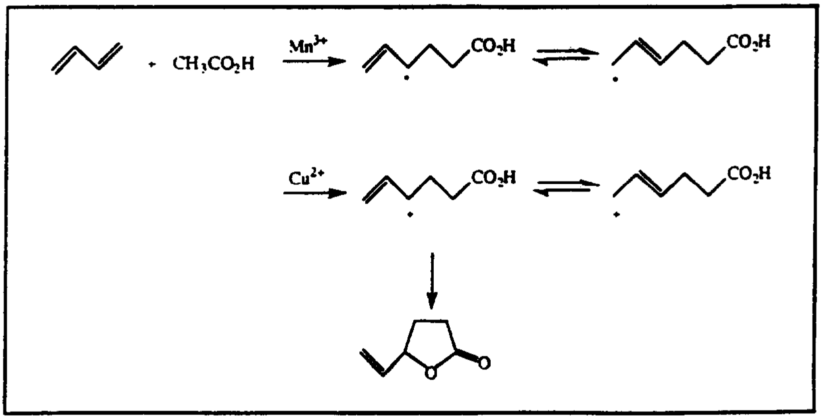
As discussed above[14], acetic anhydride is oxidized more readily by manganese(III) than is acetic acid and copper(II) is believed[16] to oxidize the intermediate radical

adducts (V) and (VI) to cations (VII) and (VIII) more efficiently than manganese(III) (Scheme 5), thus preventing free radical-initiated polymerization of butadiene, as has been previously reported under Kolbe conditions.[17]



Scheme 5

In the absence of acetic anhydride the intermediate cation may cyclize, instead of reacting with acetate as the nucleophile, and thus a different product, the lactone, results (Scheme 6).



Scheme 6

With these encouraging exploratory results, and having shown that (III) and (IV) might be converted into sorbic acid under acid catalysis, a development study of this reaction seemed warranted.

For our initial development effort, we utilized a 600 ml. Parr autoclave equipped with a glass liner, thermocouple, mechanical stirrer (Teflon®), graphite anode and a graphite cathode wrapped with porous Teflon® (Zitex®), to minimize back reduction of manganese(III). Results are shown in Table 1. Run (1), using pressurized butadiene and a current density of 16 mA/cm^2 gave a respectable 59% current efficiency for distilled acetoxyhexenoic acids. An insulating deposit was found to have formed on the anode, causing the applied voltage to rise during the run.

Run (2), at atmospheric pressure, gave a significantly lower current efficiency in this cell.

Mass transport was improved by switching to vigorous gas circulation (*ca.* 2 l/min.) in run (3) and current efficiency reached the highest value thus far attained.

Doubling the current density to 32 mA/cm^2 in run (4) caused only a slight loss in efficiency for acetoxyhexenoic acid formation but a significant new problem became apparent when a gas analysis was carried out at the end of the reaction. In the undivided cell, to our surprise, butadiene was being cathodically reduced to mixed butenes with almost 90% current efficiency. Whilst this could be tolerated in a laboratory preparation, for an industrial process, it represents a major loss of a primary raw material and as such had to be avoided.

Further work indicated that butadiene was undergoing an electrocatalytic hydrogenation on the copper metal freshly deposited on the cathode surface *via* reduction of our copper(II) co-catalyst.

This reduction, which we were unable to eliminate completely, prompted us to look at divided cell operation, as discussed further below.

Run (5) underlines the contribution of the copper co-catalyst: current efficiency falls dramatically in its absence. Run (6) shows the contribution of cathode shielding in cutting down back-reduction.

B. Flow Cells

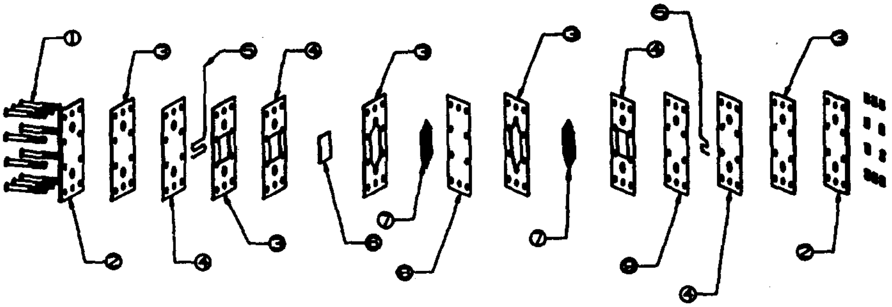
A separate chemical study showed that, in spite of the disappointing result (Table (1), run (2)) obtained with the electrochemical reaction at atmospheric pressure, it was possible to obtain an 80% yield of acetoxyhexenoic acids from previously prepared manganese(III). We, therefore, attributed the low yield in the electrochemical reaction to insufficient mass transport, caused by poor cell geometry, and set out to build a better cell for atmospheric pressure operation.

Our first approach was to construct a conventional plate and frame, divided cell with a Nafion® membrane as shown in Figure (II). Anolyte and catholyte were pumped from steam-jacketed, glass resin kettles and butadiene was sparged into the anolyte at

TABLE (1) Synthesis of Acetoxyhexenoic Acids in Pressurized Batch Reactor

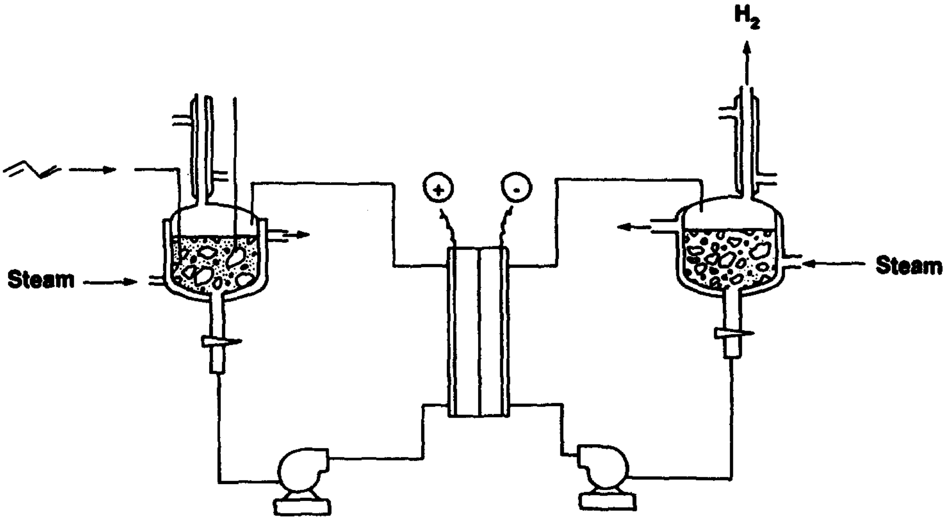
Run No.	Electrolyte (g)	Temp. °C	Pressure psig	Current mA	Voltage v.	Time hr.	Current Efficiency %	Comments
1	AcOH(110), Ac_2O(110), NaOAc(25), $Cu(OAc)_2$(3.7) $Mn(OAc)_2 \cdot 4H_2O$(12.5) Butadiene (27)	95	66-177	500	13.6-19.0	18	59	Mechanical stirring
2	As above, except butadiene	95-100	1 atm.	500	19.5-32	18	35	Atmosheric pressure gave low current efficiency.
3	As run (1)	95	56-177	500	15.6	18	78	Gas stirring (3)-(6)
4	AcOH(147 ml) Ac_2O(73 ml) NaOAc(25) $Mn(OAc)_2 \cdot 4H_2O$(12.5) $Cu(OAc)_2$(3.7) Butadiene(28.4)	95	74-126	1000	30-32	6.25	73	C.D.= 32 mA/cm^2 Butenes quantified at 87% CE. 90% Butadiene balance
5	Repeat of (1) without $Cu(OAc)_2$	97	56-76	500	18.5-23.5	9.4	23	"Manganese only" gives low current efficiency
6	AcOH(200 ml) Ac_2O(40 ml) others as (1)	95	80-86	500	14-12	21.4	33	"Unshielded" cathode → back-reduction and low current efficiency

Figure (II) Divided, Atmospheric Pressure Flow Cell



1. 10-24 bolts with Teflon® insulating sleeves
2. Steel backplate (13 cm x 22 cm x 1/4")
3. Teflon® spacer (1/8")
4. Neoprene gasket
5. Contact wire
6. Anode
7. Polyethylene mesh turbulence promoter
8. Nafion® membrane
9. Steel cathode (1/16")

Figure (III) Divided, Atmospheric Pressure Cell-Flow System



atmospheric pressure, and 98°C, to give a saturated solution *ca.* 0.1 molar in butadiene (Figure III).

Initial results with this cell are shown in Table (2). A couple of early runs at a current density of 14 mA/cm^2 (linear flow rate 0.77 m/s) with no turbulence promoter on the anode gave severe anode fouling which caused the reaction to be shut down. Elemental analysis of the insulating material on the anode indicated it to be a butadiene-acetic acid polymeric material. Incorporating polyethylene mesh turbulence promoters gave the first successful run (Run (7) Table (2))

Table (2) Synthesis of Acetoxyhexenoic Acids in Divided, Atmospheric Pressure, Flow Cell

Run No.	Current AMPS	Time Hours	Current Density mA/cm^2	Graphite Anode Type[a]	Anolyte[b] Flow l/min.	Current[c] Efficiency %	Comments
7	1.6	30	29	AGSX	2.7	71	Anode partially fouled
8	1.6	20	29	ECL	2.7	71	Less fouling
9	5.0	8.25	125	FELT	1.15	76	High current density OK
10	6.5	7.4	163	FELT	1.15	73	1st of series
11	6.5	7.4	163	FELT	1.15	73	11th run with same anode
12	5.0	6.0	125	FELT	1.15	83	95% butadiene balance, 90% selectivity
13	6.0	3.0	150	FELT	1.15	73	Cut anolyte x 2
14	5.0	12.0	125	FELT	1.15	65	Drop in C. E. *vs.* conversion
15	5.0	6.0	125	FELT	1.15	39	Precharge 100 g acetoxy-hexenoics
16	5.0	9.75	125	FELT	1.15	64	Precharge 52 g lactone
17	2.0	7.5	110	ECL	15.0	75	Flat plate anode high flow
18	3.0	5.5	166	ECL	15.0	74	Higher current density
19	4.0	4.0	220	ECL	15.0	84	Higher current density
20	4.0	5.5	220	ECL	15.0	32	Repeat run 19. Anode failed

a. AGSX and ECL graphite plate and WDF graphite felt from Union Carbide

b. $Mn(OAc)_2 \cdot 4H_2O$(0.204 mol), $Cu(OAc)_2 \cdot H_2O$(0.073 mol), KOAc(1.22 mol), AcOH(590 ml), Ac_2O (290 ml)

c. For formation of (III) + (IV); ratio of (III):(IV) = 60:40 ± 10%

In this run we used a graphite plate anode with a respectable current density of 29 mA/cm^2 (flow rate 0.7 m/s) for a current efficiency of 71% for acetoxyhexenoic acids, with only a minor amount of anode fouling observed.

Repeating this run with a different graphite anode gave a very similar result, with even less anode fouling observed (run (8)).

In order to try and eliminate the anode fouling problem completely we investigated the use of a high surface area graphite felt anode and obtained an extremely encouraging result (run (9)). At a nominal current density of 125 mA/cm^2, a realistic value for large scale operation, and a linear flow rate of only 0.3 m/s, we obtained a 76% current efficiency with no indication of anode fouling.

The same anode was then re-used for a series of eleven identical runs totalling 81 hours of electrolysis, the first and last of which are shown as runs (10) and (11). Current density for these runs was pushed even higher, to 163 mA/cm^2, and current efficiency was consistently 70-75%.

In run (12) butadiene exiting the anolyte was collected in a cold trap for quantification purposes. Total butadiene accountability was 95%, translating to a selectivity for acetoxyhexenoic acids of 90%, assuming that the missing 5% formed byproducts. Thus, selectivity on butadiene is in line with current efficiency and no major, unobserved byproducts are being formed. The problem of reduction to butenes, of course, disappears with divided cell operation.

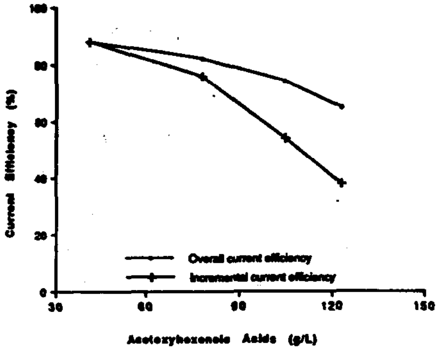
It thus appeared that the electrochemical part of this reaction system could be run under realistic conditions for commercial operation and our attention turned to a couple of other factors. In electrochemically-driven, metal-mediated reactions the ratio of sustainable current to anolyte volume is determined by the homogeneous kinetics of the mediated reaction and determines the volumetric productivity of the reactor.

Runs (10) and (11) were operated at about 6 amps/liter of anolyte giving a steady state manganese(III) concentration of 17 *mM* and a volumetric productivity of 0.11 g-mol/l/hr. In run (13) the anolyte volume was halved but the current maintained at 6 amps, giving a productivity of 0.22 g-mol/l/hr with no loss in current efficiency at the same product loading. Steady state manganese(III) concentration was 35 *mM*. Having attained this fairly reasonable level, productivity was not pushed further at this time.

In addition to volumetric productivity we were interested in the effect of product payload which determines the amount of solution to be processed for a given amount of product, thus impacting process economics.

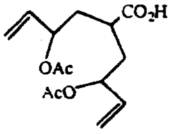
Run (14) was sampled at different times during the run and, as Figure (IV) shows,

Figure IV: Variation of Current Efficiency with Acetoxyhexenoic Acids Payload

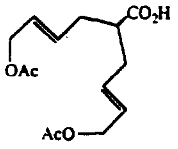


as the concentration of acetoxyhexenoic acids increases, current efficiency decreases. At low payloads the reaction is extremely efficient (>90%) but, at 100 g/l, overall current efficiency has fallen to *ca.* 75%. Beyond this concentration overall current efficiency continues to drop and incremental current efficiency, for given payload intervals, drop even more rapidly.

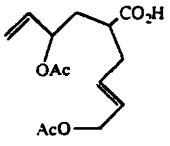
We were not too surprised at this result since we expected the acetoxyhexenoic acids to undergo a manganese(III)-mediated oxidation and subsequent addition to butadiene to give products such as (IX),(X) and (XI).



(IX)



(X)



(XI)

Byproducts of this type were not isolated but were identified by GC-mass spectrometry. Other potential high payload byproducts would include those derived from attack of acetic anhydride radicals on the olefinic bond of the acetoxyhexenoic acids and analogous reaction of two molecules of acetoxyhexenoic acid.

Run (15) which was precharged with the acetoxyhexenoic acids showed a drastic reduction in current efficiency for their further formation, as expected.

In run (16) we precharged a comparable molar amount of γ-vinyl-γ-butyrolactone to the electrolysis. We expected the lactone to be somewhat more stable to further oxidation and this expectation was borne out in a 64% current efficiency. Thus, it was thought that continuous *in situ* conversion of the acetoxyhexenoic acids into lactone might represent a method of improving selectivity at high payloads.

Finally, in order to investigate the limits of graphite plate electrodes, the anolyte tubing was increased from 1/4" diameter to 1/2" diameter, allowing a much higher pumping rate, up to 15 l/min. At this flow rate estimated linear velocity across the anode was *ca.* 4 m/sec. Coupled with the use of a turbulence promoter this allowed us to carry out run (17) at 110 mA/cm^2, on a plate of ECL graphite, giving a normal current efficiency and no anode fouling. Similarly, run (18) at 166 mA/cm^2 gave no problems, but a further increase to 222 mA/cm^2 (runs (19) and (20)) finally caused the anode to fail, and Kolbe products to form.

Thus, commercially acceptable current densities had been demonstrated on both graphite plate and graphite felt anodes.

Stability of operation was demonstrated when both graphite plate and felt electrodes were run in a repetitive batch mode for 1000 hours of electrolysis time at 80 mA/cm^2 with a current efficiency averaging about 80%.

C. *In Situ* Formation of γ-Vinyl-γ-butyrolactone

Although we had thus far obtained better yields in reactions giving the acetoxyhexenoic acid mixture, the lactone was felt to be a more desirable product for several reasons, namely:

- greater stability towards further oxidation
- no formation of salts or mixed anhydrides
- easier purification by distillation
- no acetic acid byproduct on subsequent conversion into sorbic acid in an aqueous system.

We, therefore, screened a number of catalysts for conversion of the acetoxyhexenoic acids into lactone, in the electrolysis solution. Low level catalytic activity was shown by the acetates of silver, mercury(II), zinc or nickel; modest activity by platinum on carbon but the best activity, fortuitously, was exhibited by copper(I) acetate, formed initially by addition of copper powder to the reaction mixture where it dissolved on disproportionation with copper(II) in solution.

Table (3) shows some of the results we obtained and our major observations may be summarized as follows: high selectivities (79%) are attainable but the reaction appears to equilibrate at about 90% conversion. Potassium acetate electrolyte is necessary for efficient conversion but manganese(II) has little effect. Electrolysis solutions appear to contain some copper(I), as a result of the primary redox reactions, but its catalytic activity may be largely removed by exposure to air.

Table (3) Conversion of Acetoxyhexenoic Acid Mixture into γ-Vinyl-γ-Butyrolactone

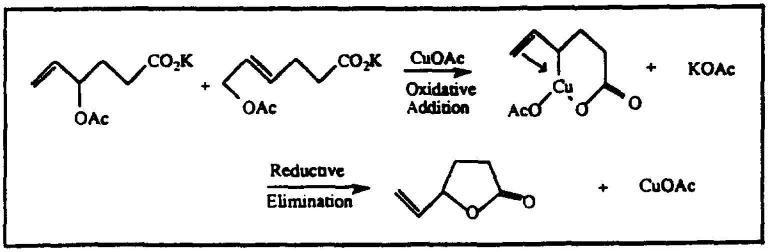
Solution %	Catalyst	Time hrs.	Temp. °C	Conversion %	Mass Balance %	Selectivity to lactone -
"Synthetic"[a]	None	6.0	125	17	86	16
"Synthetic"	Cu(0.3 g)	3.0	125	82	95	94
"Synthetic" minus Mn(OAc$_2$) & KOAc	Cu(0.3 g)	3.0	125	16	91	46
"Synthetic" minus Mn(OAc)$_2$	Cu(0.3 g)	3.0	125	79	87	84
Anolyte[b]	None	6.5	125	81	100	94
Anolyte + oxygen	None	6.0	125	21	93	42
Anolyte	Cu(0.3 g)	1.5	125	86	100	96

a. $Mn(OAc)_2 \cdot 4H_2O$ (20 g); $Cu(OAc)_2 \cdot H_2O$(2.0 g); KOAc(50 g); AcOH(750 ml); Ac_2O(250 ml). 50 g Aliquots of this solution + 5.0 g mixed acetoxyhexenoic acids.

b. $Mn(OAc)_2 \cdot 4H_2O$(150 g); $Cu(OAc)_2 \cdot H_2O$(43.8 g); KOAc(700 g)*; AcOH(1680 ml); Ac_2O(870 ml). Electrolysed 115 amp-hours to give 280 g acetoxyhexenoic acids. 50 g aliquots used.

* Total added during run: transports to catholyte during electrolysis.

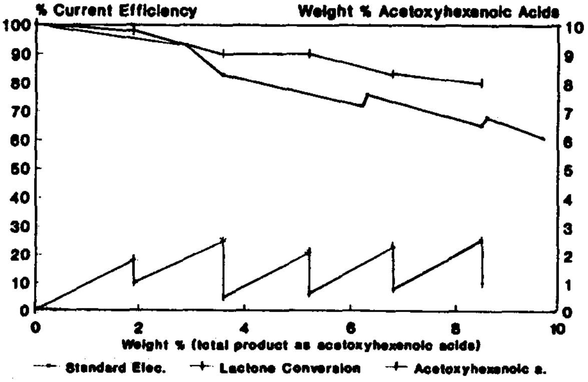
We did not carry out any mechanistic studies on this reaction but it seems likely that a formal copper(I)-copper(III) transition, previously implicated in other copper(I)-catalyzed reactions[19], is involved, as suggested in scheme (7).



Scheme 7

It was a relatively easy matter to generate copper(I) catalyst and form lactone (II) during a batch electrolysis with the divided flow cell system. With the addition of two reactors to the flow system in Figure (III), one to act as a holding tank and the other fitted with two small graphite electrodes, we were able to generate small, controlled amounts of copper(I), electrolytically, in a batch of solution which had previously been electrolyzed to form acetoxyhexenoic acids. This then catalyzed the formation of lactone in the first batch of solution while a second batch was electrolyzed to form acetoxyhexenoic acids. Using the holding tank the two batches of solution were then interchanged and, by a repetition of this procedure, the concentration of lactone was built up in a stepwise procedure. Figure (V) shows the results of a run such as this, confirming the improvement in overall current efficiency obtained *via* the lactone.

Figure V. Comparison of Standard Electrolysis with Semi-Continuous Conversion to Lactone (5 cycle).



CONCLUSIONS:

We have demonstrated in this work that it is possible to carry out the electrochemical oxidation of manganese(II) to manganese(III), in acetic acid, in a manner sufficiently practical and efficient to support large scale synthesis. In the absence of conflicting complications from accompanying chemistry, an undivided cell may even be used.

For the specific reaction of interest, between butadiene and acetic acid to give sorbic acid precursors, we have taken a rather inefficient, awkward, high pressure, stoichiometric reaction and developed it into an electrochemically-mediated sequence, catalytic in manganese(II) at atmospheric pressure. The result is an efficient, practical system, suitable for scaleup and with which many kilograms of product were produced.

A robust electrolysis system using graphite plates, or the more resilient graphite felt anodes, was operated successfully. Nafion® membrane was shown to function extremely well in this aggressive, non-aqueous medium. Other suitable materials of construction included polypropylene, Ryton® and zirconium; stainless steel and Hastelloy are corroded by this medium.

The use of a divided cell was necessitated by the unexpected and efficient reduction of butadiene to butenes at the cathode. This was concluded to be an electrocatalytic process, taking place on the surface of the copper deposited on the cathode surface by reduction of the cupric acetate cocatalyst.

The identity of our product changed a couple of times. In the reaction as initially reported γ-vinyl-γ-butyrolactone was formed directly but in low yield. Our first series of modifications changed the course of the reaction to produce a mixture of acetoxyhexenoic acids and improved the yield significantly. Even further overall yield improvements were then demonstrated by converting the acetoxyhexenoic acids into the more stable lactone as the reaction proceeded, using a copper(I) catalyst. It was concluded that this reaction took place through the intermediacy of a π-allyl copper(III) species. This catalysis by copper(I) was successfully extended to the conversion of the lactone into sorbic acid in an aqueous hydrochloric acid system[20]. Thus copper played a pivotal role throughout this reaction sequence.

By coupling the work described here[21, 22] with an improved product separation method[23] and improvements in the conversion of the lactone into sorbic acid, all the elements of an economically attractive route to sorbic acid, based on the readily available butadiene and acetic acid, were demonstrated.

EXPERIMENTAL:

Synthesis of γ-Vinyl-γ-Butyrolactone: Stoichiometric Manganese(III)

Under nitrogen 115 g (0.43 mole) of manganese(III) acetate dihydrate, 24.5 g (0.35 mole) of potassium acetate and 385 ml of glacial acetic acid were charged into a 760 ml top-stirred stainless steel Parr reactor. The reactor was chilled and 43 g (0.890 mole) of 1,3-butadiene was condensed into the reactor. Stirring was begun and the reactor was heated to 140°C over 20 min. The reactor was maintained at 140°C with stirring for three hr, then cooled and vented. The product mixture, consisting of a white solid plus yellow liquid, was taken up in 210 ml of water and 100 ml of ether. The water layer was separated and extracted with three 75-ml portions of ether.

The combined ether solutions were dried over magnesium sulfate and stripped on a rotary evaporator to remove ether. The residue was distilled through a short-path microware still (bp 25-160°C @ 0.8 mm Hg) to give 25.3 g of distillate (trapped in Dry Ice) and 7.7 g of pot residue. The distillate was fractionated through a 6" Vigreux column to give 9.3 g of product (bp 97-100°C @ 15 mm Hg) of greater than 99% purity by GC analysis (6 ft. NPGS+ 1% H_3PO_4,80-240°C/12°C/min) for a 39% yield.

^{1}H nmr analysis (60 mHz, CD_3CN) showed δ 1.6-2.7 (m,4H); 4.7-6.3 (m,4H)

^{13}C nmr analysis was carried out to obtain three different spectra: (1) undecoupled (2) fully proton decoupled and (3) NOE suppressed. Chemical shifts in the undecoupled spectrum were assigned as follows δ (d_5-pyridine): 178.4 (s, C_1); 29.3 (t, C_2 and C_3); 81.9 (d, C_4); 137.8 (d, C_5); 118.1 (t, C_6). Mass spectroscopy (electron impact) showed m/e: 112 (100%), 85 (50%), 67 (33%), 57 (72%), 56 (95%), 55 (65%).

Exploratory Reaction: Modified Fisher-Porter Bottle

A 100 ml Fisher-Porter bottle was fitted with a pressure gauge, stir bar and two graphite rod electrodes connected through a Conax® insulated fitting. The electrodes were spectroscopic grade 1/4" diameter graphite rods, immersed to a depth of 2.5 inches in the electrolyte and separated by 0.5 inches in a Teflon® holder. The cathode was wrapped with Zitex® porous Teflon®. The bottle was charged with acetic acid (15 ml), acetic anhydride (15 ml), sodium acetate (2.5g), manganese(II) acetate tetrahydrate (1.25g), copper acetate monohydrate (0.27g) and butadiene (3.0g). The mixture was heated to 105-113° in an oil bath and electrolyzed at 0.1 amperes. Pressure slowly increased from 40 to 60 psig and four times during the run the mixture was vented and recharged with butadiene (3.0 g). Total electrolysis time was 10.7 hours, during which applied voltage increased from 8 volts to 13.5 volts.

At the end of the reaction, a sample was analyzed directly by GC, using *n*-nonane as internal standard (5% OV-101 on chromosorb GHP, 100°-270° at 10°/min.). Analysis showed a 58% current efficiency for γ-vinyl-γ-butyrolactone (II). It was subsequently shown (see below) that this reaction did not produce the lactone directly but a mixture of 4-acetoxy-5-hexenoic acid(III) and *trans*-6-acetoxy-4-hexenoic acid(IV). Under the conditions of this GC analysis, (III), and (IV) cyclized with elimination of acetic acid in the heated injection port to give (II). When the mixture was later re-analyzed, using the silylation procedure described below, we observed a 30% current efficiency for (III) and 21% for (IV).

Electrolysis in 600 ml Reactor

A Parr 600 ml. top-stirred autoclave was equipped with a glass liner, Teflon® stirrer, thermocouple and two graphite plate electrodes, electrical connection being made through a Conax® insulated pressure fitting.

The reactor was charged with acetic acid (100 ml), acetic anhydride (110 ml), sodium acetate (25 g), $Mn(OAc)_2 \cdot 4H_2O$ (12.5 g), $Cu(OAc)_2 \cdot H_2O$ (3.7 g) and butadiene (27 g) - from a pressurized Fisher-Porter bottle with a dip tube. Electrodes were "glass blowers' brick" graphite (St. Mary's Carbon) (3.1 x 10.2 cm; 3 cm gap) and the cathode was wrapped with Zitex® porous Teflon®.

Electrolysis was conducted at 500 mA and 95°C with mechanical stirring for 18 hours. Cell voltage increased from 13.6 to 19 V and pressure increased from 66 to 177 psig.

The cell was cooled and dismantled when a black, powdery insulating deposit was observed on the anode.

The solution was stripped at 45°C using a vacuum pump; water (100 ml) was added to the residue and the mixture was extracted with ether (2 x 100 ml). The combined ether extract was washed with saturated sodium chloride solution (20 ml) to remove traces of copper, dried ($MgSO_4$) and evaporated to leave 24.8 g of residual liquid. GC analysis (trimethylsilylated sample, 10% SE52/Chromosorb 80-240°C at 10°/min.) showed two major components in the ratio 57:43.

A portion of the residue (20.8 g) was distilled (103-109°C/0.05 mm Hg.) to give 15.2 g of colorless liquid, identified as the mixture of acetoxyhexenoic acids (see below), corresponding to a current efficiency of 59%.

Elemental analysis of the mixture was as follows:
Calculated for $C_8H_{12}O_4$: C, 55.80; H, 7.03; O,37.17
Found: C, 55.87; H, 7.03; O, 37.12

Fractional distillation of the mixture gave the major component (A) b.pt. 98-102°C/0.05 mm Hg and minor component (B) b.pt. 110-114°C/0.05 mm.Hg. Component (B) crystallized on standing to give a white solid, m.pt. 40-40.5°C.

Nmr analysis (60mHz) of component (A) gave: δ 2.0, (s,3H); 2.2-2.6(m, 4H); 5.0-6.1(m,4H); 11.1(s,1H).

Component (B) showed: δ 2.0(s,3H); 2.4 (broad, 4H); 4.5(d,2H,J=4Hz); 5.5-5.8(m,2H); 11.2 (s,1H).

Mass spectrometry (electron impact) of component (A) showed m/e: 43 (100%); 45 (41%); 55 (45%); 67 (59%); 71 (52%); 84 (39%); 111 (70%); 112 (58%); 113 (74%).

Component (B) showed m/e: 43 (100%); 67 (62%); 70 (71%); 84 (61%); 112 (42%); 113 (27%).

High resolution nmr for component B (Varian VSR300): δ 2.00(s, 3H); 2.40(m, 4H); 4.49(d, 2H); 5.68(ABXY, 2H, J_{AB}=15.4 Hz).

On the basis of this analytical data component (A) was concluded to be 4-acetoxy-5-hexenoic acid(III) and component (B) *trans*-6-acetoxy-4-hexanoic acid(IV). The *trans* assignment was based on the olefinic hydrogens' coupling constant.

GC Analysis of Electrolysis Solutions:

The most reliable analysis for acetoxyhexenoic acids involved preparing the trimethylsilyl derivatives. This method was applicable either to the isolated compounds or directly to electrolysis solutions. For electrolysis solutions the procedure was as follows.

To 1 ml of electrolysis solution was added *ca.* 5 wt. % benzophenone as internal standard. Water (0.15 ml) was then added and the solution heated in a sealed vial at *ca.* 100°C for 20 minutes to hydrolyze anhydrides. This solution (0.1 ml) was then added to Regisil® (1 ml; BSTFA = 10% TMCS) and again heated in a sealed vial at *ca.* 100°C for 20 minutes. The sample was then analyzed on a 10% SE52/100-120 mesh high performance chromosorb column, 80-240°C programmed at 10°C/min. This analysis also quantified γ-vinyl-γ-butyrolactone.

Divided, Atmospheric Pressure Flow Cell

As shown in Figures (II) and (III), the plate-and-frame divided electrochemical cell was constructed of stainless steel back-plates with Teflon® gaskets used to form the anolyte and catholyte passages. Anode and cathode surfaces were 6 cm x 15 cm with inlets at each end of the longer dimension. Inlet and exit were tapered at about 45° to aid streamlined flow. The anolyte and catholyte compartments were separated by a membrane of Nafion®425. Spacers provided 1/8" of gap between the membrane and each electrode such that the overall cell gap was 1/4". Within each compartment was a mesh of polyethylene with approximately 1/4" square grids and having a thickness of ~1/8" (CONWED XN-5050). The mesh rested against the electrodes, masking each such that the effective area of each electrode was about 40 cm^2. Each cell compartment was connected by pumps and piping to its own steam heated reservoir. Gaseous 1,3-butadiene was sparged into the anolyte continuously, maintaining a saturated solution of the diene.

(A) Felt Anode

In the above equipment, an anode of Union Carbide WDF graphite felt (~1/4" thick) and a cathode of stainless steel were used. An anolyte solution consisting of

$Mn(OAc)_2 \cdot 4H_2O$	50 g (204 mmol)
KOAc	150 g (1.53 mol)
$Cu(OAc)_2 \cdot H_2O$	14.6g (73 mmol)
HOAc	590 ml
Ac_2O	290 ml

and a catholyte consisting of

KOAc	120 g (1.22 mol)
HOAc	880 ml
Ac_2O	35 ml

were charged into their respective reservoirs. The solutions were maintained at ~105°C and circulated through the cell (anolyte flow rate 1.2 l/min, for a linear rate of 21 cm/second; catholyte flow rate 0.5 l/min).

The system was electrolyzed at a constant current of 5 amps (125 ma/cm^2) (~12 volts) for three hours. After this time a sample of anolyte was taken, treated with H_2O, and silylated with Regisil® (Regis Chemical). GC analysis showed a total of 45.7 g of a mixture of 4-acetoxy-5-hexenoic acid and 6-acetoxy-4-hexenoic acid corresponding to a current efficiency of 95%.

55 g (561 mmol) of KOAc was added to the catholyte and the system was electrolyzed for 3 hours at 5 amps. An anolyte sample analyzed by GC as above showed 80.5 g of the mixture of acetoxyhexenoic acids corresponding to an overall current efficiency of 84%. The anolyte was distilled under reduced pressure to remove most of the acetic acid and acetic anhydride. 100 ml of water was added and the mixture was again distilled to remove most of the liquids. The residue was dissolved in a minimal amount of water and extracted 3x with diethylether. The dried ether solution was distilled under reduced pressure to give 106 g of residue, shown by GC to contain 79.8 g. of a mixture of the acetoxyhexenoic acids. This corresponds to a current efficiency of 83%.

(B) Effect of Payload Increase:

The above reaction was repeated, continuing the electrolysis for a total of thirteen hours. At the end of each three hour period, 55 grams of potassium acetate was added to the anolyte to replace that transported by the current to the catholyte. Results are shown in Table (4).

The concentration of trivalent manganese was 18 to 19 millimoles per liter during much of the reaction and 23 millimoles per liter when it was terminated.

Table (4)

Hrs. Electrolysis	Grams Acetoxyhexenoic Acids	Current Efficiency - %
3	42	88
6	79	82
12	105	73
13	128	62

(C) Graphite Plate Anode

The above reaction was repeated except that

(1) ECL (Union Carbide) flat plate graphite anode was used.
(2) No turbulence promoters were used.

An anolyte flow rate of 3 l/min. (linear flow ~34 cm/sec) was obtained. Area of each electrode was approximately 70 cm^2. The system was electrolyzed for 48 hours at a constant current of 1 amp (current density ~14 ma/cm^2). (4 volts).

KOAc was periodically added to the anolyte as above. Work-up of the anolyte solution gave 84 g of a mixture of the acetoxyhexenoic acids corresponding to a current efficiency of 58%.

(D) Graphite Plate Anode, Increased Flow

The cell used above was modified to give flow channels of 3 cm x 15 cm x 3.2 mm. The width of the flow channel was gradually tapered to about 1.25 cm wide at the ends to provide streamlined flow. Larger external piping (1/2 inch) gave a flow rate of 15 l/min (linear flow 404 cm/sec). Polyethylene mesh turbulence promoters were used, giving a working area of 18 cm^2 for each electrode. One-half the total quantity of both anolyte and catholyte used in the previous examples was charged to the reservoirs. A constant current of 3 amps (166 ma/cm^2) (17 volts) was passed for 5.5 hr. KOAc was added periodically to the anolyte as in previous examples. Results of analysis are given in Table (5).

TABLE (5)

Hrs. Electrolysis	Grams Acetoxyhexenoic Acids	Current Efficiency - %
3	19	85
4.17	32	79
5.5	40	75

Conversion of Acetoxyhexenoic Acids into γ-Vinyl-γ-Butyrolactone

Solutions were prepared as shown in Table (3) and boiled under reflux with a nitrogen blanket. Products were assayed by GC analysis after trimethylsilylation, as described above.

Electrolyses with Batchwise Lactone Formation

The system shown in Figure (3) was modified by adding a secondary reactor, an electrically heated 5-liter flask, and 5-liter holding flask to the anolyte system. The effective anode area of the cell was also increased to 65 cm^2. The secondary reactor was fitted with electrodes of Union Carbide WDF graphite felt with an area of ~28 cm^2 and a cell gap of 7 mm. The system was equipped with necessary valves to allow separate circulation of the primary and secondary reservoir pumping loops and to allow transfer between the two reservoirs and the hold tank. Thus the system allowed sequential production of acetoxyhexenoic acids in the primary reactor followed by conversion of these acids to γ-vinyl-γ-butyrolactone in the secondary system. By utilizing two anolyte charges, both processes were carried out simultaneously. An anolyte solution consisting of:

Manganese(II) acetate tetrahydrate	(150 g)
Copper(II) acetate monohydrate	(43 g)
Potassium acetate	(428 g)
Lithium acetate dihydrate	(54 g)
Acetic acid	(1400 ml)
Acetic anhydride	(1050 ml)

and a catholyte solution consisting of:

Potassium acetate	(300 g)
Acetic acid	(2410 ml)
Acetic anhydride	(90 ml)

were charged to their respective reservoirs and maintained at about 100°. The anolyte was kept saturated with 1,3-butadiene.

The system was electrolyzed for 2 hrs. at 5 amps after which time potassium acetate (40 g) was added and the anolyte was transferred to the secondary reactor. A new anolyte solution was charged to the primary reservoir and electrolyzed as above. Concurrently the

anolyte solution in the secondary reactor was subjected to 1 hr. of electrolysis at 1.0 amps and held for 1 hr. at reflux (130-135°C) to convert the acetoxyhexenoic acid product to lactone, then allowed to cool to 100°C. The original anolyte was then returned to the primary reservoir via the hold tank while the contents of the primary reservoir were transferred to the secondary reactor. The process was thus repeated until each batch of anolyte had experienced in order, 5 cycles of 10 amp•hr electrolysis and reflux treatment in the secondary reactor.

Results are compared to a "standard" electrolysis in Figure (V).

REFERENCES:

1. Keller, C. L.; Balaban, S. M.; Hickey, C. S.; and Difate, V. G., *Kirk-Othmer Concise Encyclopedia of Chemical Technology,* 1985, 1092.

2. Bose, A.; U.S. 2,484,067 1949.

3. Heiba, E. A. I.; and Dessau, R. M., U.S. 4,175,089 1979

4. Tsujino, Y.; Miyashita, M.; and Hashimoto, T., U.S. 4,022,822 1977.

5. Hessel, L. W.; "Manganic Acetate in Anhydrous Acetic Acid," *Bronder-Offset,* Rotterdam, 1968, Ch. 3.

6. (a) Weinberg, N. L.; "Technique of Electro-Organic Synthesis," Part 1, *John Wiley and Sons,* New York, 1974, p. 251.
   (b) Bellamy, A. J., *Acta Chem. Scand.*, B33, 1979, 208.
   (c) Bellamy, A. J.; and Simpson, B. R., *Chem. and Ind.*, May, 1981, 328.
   (d) Wagenknecht, J. H.; Coleman, J. P.; Hallcher, R. C.; McMackins, D. E.; Rogers, T. E.; and Wagner, W. G., *J. Appl. Electrochem.*, 13, 1983, 535.

7. Clarke, R.; Kuhn, A. T.; and Okoh, E., *Chem. in Brit.*, 11, 1975, 59.

8. Kramer, K.; Robertson, P. M.; and Ibl, N., *J. Appl. Electrochem.*, 10, 1980, 29.

9. Dombroski, M. A.; Kates, S. A.; and Snider, B. B., *J. Amer. Chem. Soc.*, 112, 1990, 2759.

10. Fristad, W. E.; Peterson, J. R.; Ernst, A. B.; and Urbi, G. B., *Tetrahedron,* 42, 1986, 3429.

11. Bush, Jr., J. B., and Finkbeiner, H., *J. Amer. Chem. Soc.*, 90, 1968, 5903.

12. Heiba, E. A. I.; Dessau, R. M.; and Rodewald, P. G., *J. Amer. Chem. Soc.*, 96, 1974, 7977.

13. deKlein, W. J., *Rec. Trav. Chim.*, 96, 1977, 22.

14. deKlein, W. J., *Rec. Trav. Chim.*, 94, 1975, 48.

15. Nishiguchi, I.; Hirashima, T.; and Matsubara, Y., *Electrochem. Soc. Meeting,* Oct. 19, 1987, Abst. 1349.

16. Anderson, J. M.; and Kochi, J. K., *J. Amer. Chem. Soc.*, 92, 1970, 2450.

17. Smith, W. B.; and Gilde, H.; *J. Amer. Chem. Soc.*, 83, 1961, 1355.

18. Ho, S. V., *J. Appl. Electrochem.*, 17, 1987, 398.

19. Cohen, T.; Berninger, R. W., and Wood, J. T., *J. Org. Chem.*, 43, 1978, 837

20. Coleman, J. P., and Hallcher, R. C., U.S. 4,460,787, 1984.

21. Coleman, J. P.; Hallcher, R. C.; and McMackins, D. E., U.S. 4,672,140, 1987.

22. Coleman, J. P.; Hallcher, R. C.; Rogers, T. E.; and McMackins, D. E., U.S. 4,526,990, 1985.

23. Coleman, J. P., and McMackins, D. E., U.S. 4,564,689, 1986.