Permeable Membrane Mass Spectrometry of Products of Electrochemical Oxidation of Carboxylate Ions

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The volatile products of Kolbe oxidation of carboxylate ions in water and Me₂SO solvents have been detected by permeable membrane mass spectrometry (PERMS). Deconvolution of the mass spectral data by factor analysis allows estimation of carbon dioxide, oxygen, and ethane during the course of electrolysis. In water solutions, electrolysis of water occurs in competition with the Kolbe oxidation, and it is possible to follow the individual current efficiencies for these two processes as a function of potential. In Me₂SO solutions, the oxidation of propionate and acetate led to the same products, CO_2 and ethane, but in different stoichiometric proportions. Efficiencies for ethane production are twice as large for propionate as for acetate.

The identification and measurement of many known and unknown species generated during an electrochemical experiment can be made by mass spectrometry (1-4). Permeable membrane mass spectrometry (PERMS) provides a method for selectively sampling solutes in a polar condensed phase by single-stage extraction, directly into the source vacuum of a mass spectrometer (4-10). When two or more components permeate the semipermeable membrane, the composite spectrum must be separated into a spectrum for each component of the mixture to be analyzed. A block diagram of the steps involved is shown in Figure 1.

Several general techniques are available for deconvolution of spectra, including mass spectra (11). Of these methods factor analysis (12) offers the advantage that under certain conditions neither the presence nor the identity of the species contributing to the composite spectrum need be known prior to analysis.

In an electrochemical experiment, changes in electrode surface concentrations of the reactants and products are produced directly by variation of the electrode potential. After subtraction of the potential-independent background, the PERMS spectrum at each potential represents an analysis of a different composition of these reactants and products. Such a series of spectra containing the same components but varying in proportion is ideally suited for deconvolution by factor analysis (12).

In this paper we demonstrate the treatment of PERMS data by factor analysis. The method is applied to analysis of products of the Kolbe electrolysis under conditions where product analysis has been reported in the literature. The techniques should find immediate application to qualitative identification of products of complex electrochemical reactions. Further work may lead to a fully quantitative analysis of electrode reactions by the PERMS method.

THEORY

Electrochemical Mass Spectrometry. Mass spectral analysis of electroactive species by PERMS entails the series of steps illustrated in Figure 2. The present discussion considers the case where the slow step in this series is step 3, the time required to transport analyte through the semipermeable membrane. Step 3 is characterized by a half time, $\tau_{1/2}$, which has been estimated by Calvo et al. (10) to be 12 s for transport of ethyl 2-furoate through a 25-µm silicone rubber membrane. Although $\tau_{1/2}$ can be expected to be greater or less than this value depending on the identity of the analyte, membrane, solvent, and temperature (13, 14), we have not observed $\tau_{1/2}$ values to be less than 10 s or more than 100 s. As outlined in the discussion below, under conditions used in this work, the remaining four τ values in Figure 2 are substantially smaller than $\tau_{1/2}$ for membrane transport.

Electrode to Membrane Transport of Products. Before they can partition into the membrane, the electrochemical species that are produced at the electrode surface must be transported by diffusion and/or convection to the membrane surface. For the simplest reaction

$$0 + n e^{-} \Leftrightarrow r_1 R_1 + r_2 R_2 + \dots + r_n R_n \tag{1}$$

Nernst diffusion theory predicts (15) that the surface concentration of each of the species, R_k , is related to the electrochemical current, ι , by a relation such as

$$\iota = \frac{nFA_{e}D_{k,s}}{\delta_{k}(t)} \left[\frac{[\mathbf{R}_{k}]_{e,s}}{r_{k}} \right]$$
(2)

where $[\mathbf{R}_k]_{es}$ is the concentration of species \mathbf{R}_k at the electrode surface, n is the number of electrons transferred, F is the Faraday, A_e is the area of the electrode surface, $D_{k,s}$ is the diffusion coefficient of species, \mathbf{R}_k , in the solution, and $\delta_k(t)$ is the width of the diffusion layer.

In Figure 2 the half-time required for the concentration of R_k at the membrane surface, $[R_k]_{m.s.}$, to reach a steady state is represented as τ_m . The gold minigrid electrode used in these experiments is a thin gold foil with a highly regular pattern of square holes etched in its surface. Its backside has been affixed in intimate contact with the outer surface of a silicone rubber membrane (see Figure 3). Steady-state concentrations of species R_k are reached at the membrane surface when the rate of transport to the membrane surface from the solution equals the rate of transport away from the membrane surface toward the MS source. The time for equilibration of molecules between the solution and membrane, τ_{α} , can usually be assumed to be instantaneous.

Murray et al. (16, 17) have addressed the problem of mass transport of electrode products from the minigrid surface into the holes, where they encounter the silicone membrane surface in our experiment. To achieve transverse homogeneity on the solution side of the interface, the diffusion layer thickness, $\delta(t)$ from equation 2, must be larger than the hole dimension of the minigrid electrode. For our 750 line per inch electrode (wire thickness, 10 μ m; hole width, 24 μ m), $\delta_k(t)$ is greater than the hole width for t values longer than about 0.2 s (16, 17).

It should be recognized that the concentration at the membrane/solution interface may not be uniform over the hole surface, even when a steady-state concentration has been reached. For example, if the partition coefficient

$$K_k = \frac{[\mathbf{R}_k]_{\mathrm{m/s}}}{[\mathbf{R}_k]_{\mathrm{s/m}}} \tag{3}$$



Figure 1. Steps in PERMS analysis of electrochemical products.



Figure 2. Steps in mass transport from the electrode surface to the detector of the mass spectromemter.

is very large, virtually every time a molecule, R_k , reaches the membrane/solution interface, it will be partitioned into the membrane. Membrane regions that are very near the electrode will have higher concentrations of R_k than membrane regions near the center of the hole. Nonetheless, virtually the same time should be required to achieve steady-state membrane/solution surface concentrations as would be the case if K_k were very small and very little of the electrochemical product dissolved in the membrane. A typical case of $K_k = 1$ has been schematically presented in Figure 3.



Figure 3. Schematic diagram of diffusion profiles at the membrane/electrode interface during PERMS analysis.

Membrane Equilibration. Equation 3 describes the equilibrium concentrations at the membrane/solution interface. It will be assumed here that this equality will be achieved in times very short ($\tau < 1$ ms) relative to mass transport. This is a common assumption made in studying similar heterogeneous equilibrium processes in chromatography (18) and diffusion in polymers (19).

Membrane Transport. Once a solute has partitoned into the membrane, its transport through the membrane, into the MS source, and subsequent ionization and detection are virtually identical with PERMS applications described previously (4, 6, 9, 10, 20). When steady-state mass transport has been established at the membrane/solution interface, we may treat the membrane surface as a mosaic of small areas across any one of which the solute concentrations do not vary significantly. For each small area it can be written

 $[\mathbf{R}_{k,j}]_{s/m,ss} = B_{j,k}[\mathbf{R}_k]_{es,ss}$

and

$$K_k = \frac{[\mathbf{R}_{k,j}]_{\mathrm{m/s,ss}}}{[\mathbf{R}_{k,j}]_{\mathrm{s/m,ss}}}$$
(5)

(4)

where $B_{j,k}$ is the proportionality constant between the steady-state concentration of R_k at each small homogeneous area, A_j , and the concentration at the electrode surface.

Because the pressure at the interior surface of the silicone membrane is much less than 1 P (4, 9), the concentration of volatile solutes at the membrane/vacuum interface, $[R_k]_{m/v}$, may be assumed to be virtually zero at all times. The flux in mol cm⁻² s⁻¹ of material, R_k , through the membrane at steady state is (4, 20)

$$(\text{flux})_{k,j} = D_{k,m} \frac{([\mathbf{R}_{k,j}]_{m/s,ss} - [\mathbf{R}_k]_{m/v})}{l}$$
(6)

where l is the membrane thickness. The number of moles of species R_k emerging per second into the vacuum that can be attributed to the area, A_j , is

$$(rate)_{j,k} = A_j(flux)_{k,j}$$
(7)

Combining eq 2, 4, 5, 6, and 7 yields

$$(\text{rate})_{j,k} = \frac{A_j D_{k,m} K_k B_{j,k} r_k \delta_{ss}}{n F A_s D_{k,s} l} i_{ss}$$
(8)

or, accounting for molecules coming from each of the small areas, A_j , the total mass flow rate, F_k , of species R_k in mol s⁻¹ will be

$$F_{k} = \frac{K_{k}D_{k,\mathrm{m}}r_{k}\delta_{\mathrm{ss}}i_{\mathrm{ss}}}{nFA_{\mathrm{e}}D_{k,\mathrm{s}}l}\sum_{j=1}^{N}(A_{j}B_{j,k})$$
(9)

Source Pressure. After passage through the tubing connecting the backside of the membrane to the source of the mass spectrometer, the assemblage of molecules of all kinds produces a pressure, p, in the source. However, it is the partial pressure, p_k/p , which determines the signal that is detected as an ion current, h_k , in the mass spectrum. In Henry's law region (i.e., at very low total pressure) the partial pressure of species R_k is equal to the ratio of the flow rate of R_k into the source divided by the sum of the flow rates of all species contributing to the pressure, p.

$$\frac{p_k}{p} = \frac{p_k}{\sum\limits_i F_i} = \frac{F_k}{\sum\limits_i F_i}$$
(10)

In practice during the PERMS experiment, p is dominated by solvent, which leaks through the membrane, and by adventitious leakage of atmospheric gases (O₂ + N₂) through imperfect connections in the sampling train. Thus, the total source pressure is virtually invariant during a PERMS run and eq 11 is valid over a wide range of solute concentrations, $[\mathbf{R}_k]_{e,s}$

$$p_{k,\rm ss} = Q_k i_{k,\rm ss} \tag{11}$$

where $\iota_{k,ss}$ is the partial current producing species \mathbf{R}_k as described below.

Transport of Electrochemical Reactants to the Membrane. The electrochemical reactants, O_k , in eq 1 are present at the membrane surface before the start of electrolysis. Because the rate of mass transport (convection plus diffusion) in the solution phase is much larger than in the membrane (i.e., $\delta_{ss} \ll l$), the mass flow rate of O_k into the MS source will be approximately

$$F_k^{\circ} = \frac{K_k D_{k,\mathrm{m}}[\mathrm{O}_k]^{\circ} A_{\mathrm{m}}}{l}$$
(12)

where $[O_k]^\circ$ is the bulk concentration of O_k and A_m is the area of the membrane solution interface.

During steady-state electrolysis, $[O_k]_{s/m,ss} < [O_k]^\circ$, with the number of moles of O_k diffusing in from the bulk to area, A_j , being nearly equal to the moles diffusing out toward the electrode surface

moles
$$O_k$$
 in $= B'_{j,k}([O_k]^\circ - [O_k]_{s/m,ss})$ (13)

moles
$$O_k$$
 out = $B''_{j,k}([O_k]_{s/m,ss} - [O_k]_{e,c,ss})$ (14)

or, solving (13) and (14) for the steady state condition (moles O_k in = moles O_k out, and F^o_k is small)

$$[O_k]_{s/m,ss} = \frac{[O_k]^{\circ} + B_{j,k}[O_k]_{e,c,ss}]}{1 + B_{j,k}}$$
(15)

where $B_{j,k} = B'_{j,k}/B''_{j,k}$. When limiting electrolysis is reached ($[O_k]_{e,c,ss} = 0$), eq 15 becomes

$$[O_k]_{s/m,ss}^{lim} = \frac{[O_k]^{\circ}}{(1+B_{j,k})}$$
(16)

While equations 12-16, and others which may be derived from them, are useful in understanding a general PERMS experiment, they do not apply to the Kolbe electrolysis discussed here. The electrochemical reactants are ionic species such as acetate ion, for which K_{OAC} in eq 12 is virtually zero.

Current Efficiency for Production of \mathbf{R}_k . In general, the overall current, i_{ss} , will involve more than one electrode reaction and will produce more than one product.

$$O_1 + n_1 e^{-} \stackrel{\iota_1}{\Leftrightarrow} R_1$$
$$O_2 + n_2 e^{-} \stackrel{\iota_2}{\Leftrightarrow} R_2$$
etc.

The current efficiency for production of species \mathbf{R}_k will thus be

current efficiency for production of
$$R_k = \frac{\iota_k}{\sum_j \iota_j}$$
 (17)

and

$$\sum_{k} i_{k,ss} = i_{ss} \tag{18}$$

Combining eq 11 and 18 yields the expression

$$\frac{\sum_{k=1}^{N} P_k / Q_k}{i_{\rm ss}} = 1.00$$
(19)

This relation can be used to evaluate changes in the efficiency of production of a particular product, $P_k/i_{\rm ss}$, as a function of independent variables such as electrode potential, solution composition, electrode material, and so on.

Factor Analysis. A valid factor analysis of the data derived from a PERMS study of an electrochemical reaction assumes that the observed mass spectral ion current, $H_{j,\alpha}$ can be expressed as a linear combination of terms

$$H_{j,\alpha} = \sum_{k=1}^{N} H^{\circ}{}_{j,k} P_{k,\alpha}$$
(20)

where $H_{j,\alpha}$ is the ion current at the *j*th value of m/e obtained by analysis of mixture α , $H^{\circ}_{j,k}$ is the ion current at an m/evalue of *j* for the pure compound, \mathbf{R}_k , and $p_{k,\alpha}$ is the partial pressure of compound \mathbf{R}_k in mixture α . *N* is the total number of compounds (factors) necessary to explain the observed data.

Factor analysis (12, 21) utilizes the variance in a data matrix (D) to calculate the row matrix (C) equal to the relative concentrations of the N components, and the column matrix (R) equal to the calculated mass spectra of the N pure components, where

$$D_{j\alpha} = \sum_{k} R_{jk} C_{k\alpha} \tag{21}$$

EXPERIMENTAL SECTION

Our general techniques of permeable membrane sampling and electrochemical mass spectrometry have been described elsewhere (4, 9, 10). The probe used in this work was a modification of previous designs (see Figure 4). The probe body was a 20 cm piece of 4 mm o.d. Pyrex tubing. A small piece of stainless steel screen (75 wires/in.) was placed over the open end of the probe as a porous mechanical support for the membrane/electrode. A small piece of membrane/electrode (see preparation below) was positioned over the screen and electrically connected to a gold wire contact with silver epoxy cement. After being baked for 6 h at $70 \, ^\circ$ C, the edge of the membrane was sealed to the probe body with silicone rubber cement.

The membrane/electrode consisted of a 750 line/in. gold grid (Buckbee Mears Co.) attached intimately to a 25 μ m thick silicone rubber membrane (General Electric, Medical Products Division). A small section (1 cm²) of membrane was soaked briefly in a solution of 60% uncured silicone rubber cement and 40% toluene and then placed on a flat Teflon sheet. Excess cement was removed with a glass rod. A slightly smaller piece of gold grid



Figure 4. Construction of membrane/electrode probe for PERMS study of electrochemical products.

electrode was placed on the tacky membrane surface and smoothed lightly. Membrane/electrodes were allowed to cure overnight before removal from the Teflon sheet.

Reagents. Tetrabutylammonium hexafluorophosphate was prepared by metathesis of tetrabutylammonium iodide (Aldrich Chemical Co.) and ammonium hexafluorophosphate (Alfa Inorganics) in 95% ethanol. The resultant crystals were recrystallized twice from methanol. Me₂SO was Baker Chemical Co. spectrometric grade. All other reagents were ACS reagent grade.

Apparatus. Potential and current control were provided by a PARC Model 173 potentiostat/galvanostat.

The mass spectrometer was a Du Pont Model 21-490 singlefocusing instrument. It was operated at a source pressure of ca. 1.7×10^{-3} Pa which was maintained constant throughout a complete run. The source temperature was 190 °C. It was scanned magnetically at a rate of 5 s/decade from m/e 10 to 100 with a 100-Hz filter. The ionization voltage was 70 V and the acceleration voltage was 1000 V.

The recorder was a Bell & Howell Datagraph Model 5-134 with a chart speed of 0.5 in./s.

Procedure. The interior of the probe assembly (Figure 4) was evacuated with a roughing pump for at least 10 min prior to attachment to the MS source. After pumpdown the probe was rinsed with solvent and then immersed in the solution. During the run, all material passing through the membrane also passed through the source of the mass spectrometer.

Electrolysis was initiated by setting the current or potential to the desired value and the system allowed about 1 min to reach steady state (a time long compared to $\tau_{1/2}$, the half time for transit through the membrane). Duplicate spectra were then taken at this setting and the above procedure was repeated for all desired current or potential values. All peaks in the spectrum were measured to the nearest 0.1 mm.

Background Correction for Water. In the case of the aqueous solutions, a relatively uncomplicated analysis, the background spectrum (obtained by averaging the several spectra gathered before electrolysis began) was subtracted from each spectrum gathered during the remainder of the run. Because the measured source pressure did not vary more than $\pm 10\%$ during the run, the ion currents properly represent the partial pressures of the component ions contributing to that current. Such a subtraction procedure may result in small positive or negative fluctuations in the ion currents at m/e values where background ions make a significant contribution to the total ion current. The data so corrected formed the data matrix (D) in Table I.

Background Correction for Me₂SO. In the case of Me₂SO solutions an additional step was necessary, because Me₂SO, acetic acid and propionic acid contribute to the ion current at virtually all m/e values below 80. The data matrices in Tables V and VI were obtained by the following transformation:

$$(H_{i,\alpha})_{\rm corr} = H_{i,\alpha} - \frac{H_{63,\alpha}}{H_{63,0}}(H_{i,0})$$
(22)

Table I. Data Matrix (D), for PERMS Analysis of Oxidation Products of 0.10 M Sodium Acetate in Water at a Gold Grid Electrode

			potent	ial (V v	s. Pt wire	e)	
m/e	1,0	1.1	1.1	1.2	1.3	1.4	1.6
12	0.1 <i>ª</i>	0.4	0.8	1.2	1.6	2.0	2.2
16	0.7	2.3	4.9	8.2	12.2	17.7	17.7
17	1.1	2.9	8.3	13.3	16.4	17.1	17.3
18	6.1	16.1	46.1	74.0	91.1	95.0	96.1
28	1.1	3.7	7.7	12.2	16.5	21.1	22.5
32	1.9	5.0	18.3	43.8	106.8	161.3	191.3
43	0.1	0.3	0.6	1.0	1.3	1.7	1.8
44	7.6	26.6	54.6	87.1	117.1	149.6	159.6
45	0.3	0.9	1.9	3.0	4.1	5.2	5.6
	0.10	0.48	1.18	2.44	4.40	6.68	11.6
		(Current,	, i _{ss} (mA	$A \text{ cm}^{-2}$		
^a Io	n curi	ent val	ues, H _{j.}	α , are r	elative, w	vith units	of mm.

Table II. The Normalized (R) Matrix Representing Mass Spectra Necessary to Reproduce Data Matrix (D), in Table I

m/e	1	2	3
12	0.00	0.00	1.62
16	-0.130	2.83	10.63
17	17.98	0.01	0.00
18	100.0	0.02	0.03
28	1.75	1.16	13.90
32	0.07	100.0	-0.04
43	0.05	0.06	1.22
44	11.85	7.46	100.0
45	0.55	0.35	3.27

where $H_{i,0}$ is the mass spectrum of the background, taken when the electrochemical current equals zero.

Because the number of different current levels at which mass spectra were recorded was greater than the number of m/e values used in the analyses, the data had to be analyzed in groups of eight or nine spectra. The results obtained from the factor analyses were then smoothed so that an overlapping spectrum from each group had the same percentage of components.

RESULTS AND DISCUSSION

Acetate in Water. The background-corrected D matrix in Table I was compiled from a series of mass spectra obtained during electrolysis of a 0.100 M solution of sodium acetate in water. The controlled potential was applied to a gold grid PERMS electrode immersed in a continuously stirred solution, and a mass spectrum was recorded when the current had reached a constant value. At potentials above 1.6 V, formation of bubbles on the electrode was observed and analysis results were erratic.

Simple inspection of the R matrix (Table II) derived by factor analysis of these data allows identification of the three components whose spectra are necessary to explain the observed variation in the composite PERMS spectra. They are CO_2 , O_2 , and H_2O . Notably absent is the possible dimerization product, ethane.

Factor analysis also yields the C matrix in Table III, which estimates variation of the relative partial pressures, P_j , of these three components in the MS source. Previous studies (22) have indicated that oxidation of acetate at gold in this medium occurs by a carbonium ion mechanism, yielding CO₂ but no hydrocarbon products. Oxidation of solvent water is undoubtedly responsible for the appearance of oxygen. If oxygenated products such as ethanol or formaldehyde are produced during electrolysis, this PERMS technique combined with factor analysis does not identify them. We discuss the

Table III. The Final Normalized (C) Matrix, Representing Partial Pressures of the Components of (R) for the Seven Analyses (Columns) of (D) in Table I

component r	10.						
1	7.99^{a}	21.10	60.39	96.93	119.3	124.4	125.9
$\overline{2}$	2.13	5.60	20.48	49.02	119.5	180.6	214.1
3	8.80	31.72	62.38	98.02	128.4	165.1	174.8
^a Partial press	sures are in mm	, proportional	to their contrib	oution to the io	n current, $H_{i,\alpha}$		

Table IV. Product Efficiencies and Current Efficiencies for Oxidation of 0.1 M Acetate in Water

Ε.	÷	product efficiencies		current et	fficiencies	$\frac{2}{2}$	· /·
V vs. SCE	mA/cm ²	$\overline{P_{\mathrm{CO}_2}/i_{\mathrm{o}}}$	P_{O_2}/i_o	$\overline{i_{\rm CO_2}/i_{\rm o}}$	i_{O_2}/i_o	$\frac{\sum l_j / l_0}{j=1}$	¹ CO ₂ / ¹ O ₂
1.0	0.10	(88)	(21)	(0.95)	(0.56)	(1.5)	(2)
1.1	0.48	66.1	11.7	0.71	0.31	1.02	2.3
1.2	1.18	52.8	17.4	0.57	0.46	1.03	1.2
13	2.44	40.2	20.1	0.43	0.52	0.95	0.80
14	4.40	29.2	27.1	0.32	0.71	1.03	0.45
1.5	6.68	24.7	27.0	0.27	0.71	0.98	0.38
1.6	11.6	15.1	118.5	0.16	0.49	0.65	0.33

variation of H_2O below as an uncorrected component of the PERMS background.

The ratios $P_{\rm CO_2}/i_0$ and $P_{\rm O_2}/i_0$ in Table IV vary with i_0 in such a manner that the data from at least these two species must be combined to account for the measured i_0 . In any potential region where Kolbe electrolysis and water oxidation are the only potential varying currents, values of Q_1 and Q_2 may be found which result in a constant value of 1.0 for the sum on the left-hand side of eq 19. Values of 0.0108 and 0.0263 were calculated for $1/Q_1$ and $1/Q_2$, respectively, by best fit to our measured P_j data from 1.1 to 1.5 V. The resultant current efficiencies for production of CO₂ and O₂ are summarized in Table IV and Figure 5.

The constancy of the sum of these current efficiencies is consistent with an n value of 2 in eq 1. The data at 1.0 V were neglected because of the large uncertainty in i_0 , $P_{\rm CO_2}$, and $P_{\rm O_2}$ at these low levels. At the highest voltage studied, the current efficiencies calculated are inconsistent with eq 18. This may be a consequence of bubble formation resulting in changes in the Q values. The consistency of the ratio $i_{\rm CO_2}/i_{\rm O_2}$ would indicate however, that the ratio Q_2/Q_1 does not vary detectably, suggesting the partition and mass transport of CO₂ and O_2 are affected similarly by the formation of bubbles at the interface. The maximum value of current efficiency for CO₂ production occurs at the lowest current density-an unfavorable situation for optimization of Kolbe electrolysis. At the highest current densities, the ratio $i_{\rm CO_2}/i_{\rm O_2}$ approaches a value of approximately 0.3, which may represent the ratio of electron transfer limited rates for production of these two products when the applied potential is substantially positive of the formal potentials of both couples.

The practical value of information on the current efficiencies is obvious. Simple PERMS studies of this type could lead directly to optimization of such parameters as current efficiency or power efficiency $i_j/(i_0 \times V_{cell})$ with respect to electrolysis potential, current density, solvent, background electrolyte, electrode material or pretreatment, or other independent parameters. Scale-up to macroscopic electrolysis conditions can be reasonably delimited by the range of electrolysis conditions found most efficient in a PERMS study.

Background Correction for Water. The factor analysis described above identifies water as a species that varies with the applied potential of the gold electrode. Because water is the solvent and a major component of the background PERMS spectrum, caution must be exercised in interpreting these data. We have considered three possible explanations. Water may permeate the membrane in chemical combination



Figure 5. Current efficiency vs. current density for the PERMS measured production of $CO_2(\Phi)$ and $O_2(X)$ from 0.1 M acetate ion in water at a gold electrode.

with one of the other detected species (CO₂ or O₂). The membrane permeability to water may be affected by application of a potential (or current) to the gold electrode attached to its outer surface. Alternatively, the ionization efficiency of the MS source toward water could be affected by the presence of the other species (such as CO₂ or O₂) permeating the membrane during the PERMS electrolysis experiment.

At the present time, we are unable to either prove or disprove any one of these speculations. The first explanation seems unlikely however because, in a separate study by PERMS analysis of CO₂ produced chemically in aqueous solutions (23), no relationship is observed between the solution concentration of CO₂ and ion current at m/e 18 in the PERMS spectrum. Similarly, we have been unable to verify the the second explanation by detecting similar changes in the background spectrum (principally due to water) as a function of applied potential under conditions when no electrolysis occurs.

We have therefore treated the potential dependent variation of the water spectrum in our PERMS electrolysis experiment as an uncorrected component of the background. It is an inherent strength of the PERMS experiment combined with factor analysis, that quantitative information is obtained without prior identification of the exact species necessary to make up the mixed mass spectra. Thus positively identified components, such as water in this case, may be either included

Table V. Data Matrix for PERMS Analysis during Oxidation of 0.01 M Sodium Propionate, 0.01 M Propionic Acid, and 0.1 M TBAHFP in Me₂SO Solvent

							curre	ent den	sity, m.	A/cm ²						
m/e	20	40	60	80	100	120	140	160	180	200	220	240	260	270	280	290
15	0.7 <i>ª</i>	1.0	1.5	2.0	2.4	2.8	3.1	3.2	3.2	3.3	3.3	3.4	3.7	4.1	4.3	4.8
27	0.2	0.5	0.6	0.9	1.1	1.4	1.5	1.7	1.8	1.8	1.9	2.1	2.2	2.7	3.6	4.2
28	7.8	15.9	21.8	29.7	37.5	45.2	50.9	55.4	59.9	61.8	64.7	69.6	74.1	89.1	116.6	139.1
29	1.3	2.6	3.6	5.0	6.1	7.4	2.4	9.1	9.8	10.1	10.6	11.4	12.1	14.7	19.1	22.8
30	0.4	0.9	1.2	1.7	2.1	2.5	2.9	3.1	3.4	3.5	3.6	3.9	4.1	5.0	6.5	7.8
44	1.0	2.0	3.9	5.0	6.0	6.7	7.2	7.6	7.8	8.6	9.0	10.6	13.0	18.0	22.6	27.5
46	1.7	2.5	3.8	4.9	5.9	6.9	7.8	8.1	8.1	8.2	8.2	8.6	9.3	10.1	10.7	12.0
47	5.0	7.3	11.1	14.4	17.4	20.3	23.0	23.8	23.9	24.0	24.2	25.3	27.3	29.8	31.6	35.3
48	2.2	3.2	4.8	6.3	7.6	8.8	10.0	10.4	10.4	10.5	10.5	11.0	11.9	13.0	13.8	15.4
76	1.8	1.2	4.0	5.2	6.3	7.3	8.3	8.6	8.6	8.6	8.7	9.1	9.8	10.7	11.4	12.7
^a Pea	k heigh	nts in m	m.													

Table VI. Data Matrix for PERMS Analysis during Oxidation of 0.025 M Sodium Acetate, 0.025 M Acetic Acid, and 0.1 M TBAHFP in Me₂SO Solvent

	current density, mA/cm ²													
m/e	20	40	60	80	100	120	140	160	180	200	220	240	260	280
15	0.7 <i>ª</i>	1.6	2.9	4.4	5.7	6.8	8.0	8.9	9.8	10.5	10.7	10.2	9.3	8.4
27	0.2	1.1	2.1	3.1	3.9	4.6	5.3	5.6	5.8	5.9	6.0	6.3	7.0	8.8
28	3.2	16.2	30.8	45.3	56.6	66.4	76.1	80.9	83.4	85.8	87.4	90.6	102.0	127.9
29	0.6	2.8	5.4	8.0	9.9	11.6	13.4	14.2	14.6	15.0	15.3	15.9	17.9	22.4
30	0.2	1.0	1.9	2.8	3.5	4.1	4.7	5.0	5.1	5.3	5.4	5.6	6.3	7.9
44	1.0	1.8	2.5	3.2	4.0	4.9	5.8	6.5	7.2	8.1	9.0	9.9	11.6	18.5
46	0.7	1.6	2.9	4.3	5.6	6.7	7.9	8.8	9.7	10.4	10.6	10.1	9.2	8.4
47	2.2	5.0	8.8	13.2	17.2	20.5	24.0	26.8	29.5	31.8	32.2	30.8	28.0	25.5
48	0.9	2.0	3.5	5.3	6.9	8.3	9.7	10.8	11.9	12.8	13.0	12.4	11.3	10.3
76	0.8	1.7	3.0	4.6	6.0	7.9	8.3	9.3	10.2	11.0	11.2	10.7	9.7	8.8
^a Peak	height	in mm.												

Table VII.	R Matricies for Propionate	e and Acetate	Oxidation in Me ₂ SO	
	-			

	propion	ate oxidation con	ponents	acetate oxidation components				
m/e	1	2	3	1	2	3		
15	0.0	33.1	0.1	14.1	0.6	-0.2		
27	0.2	0.2	6.9	-0.2	0.6	3.1		
28	11.0	2.3	100.0	4.6	18.0	100.0		
29	1.3	0.2	17.6	1.5	4.8	15.8		
30	0.7	0.1	6.2	0.1		5.9		
44	100.0	0.0			100.0			
46	1.2	32.9		34.1	1.0	0.6		
47	1.8	100.0		100.0	0	2.1		
48	0.9	40.3		43.5	0.4	0.8		
76	0.7	34.9		36.3	0.5	0.1		
assigned species		solvent	C_2H_6	solvent		C_2H_6		

in or excluded from the interpretation of the electrochemical data based on criteria independent of the mass spectral experiment.

Carboxylate Ions in Me₂SO. Background corrected D matrices compiled from PERMS analysis of propionate and acetate oxidation in Me₂SO are shown in Tables V and VI. The corresponding R and C matrices derived by factor analysis of these data are shown in Tables VII and VIII. In both cases the Malinovskii IND function (12) indicates that three components are necessary to account for the observed variation of the mass spectra with current density. Inspection of the R matrices suggests that CO_2 and C_2H_6 are produced by electrooxidation of both these carboxylate ions, although our analysis below indicates that the mechanisms are somewhat different.

Each R matrix also contains a third species of uncertain identity with a base peak at m/e 47. A search of the Mass Spectral Research System data base suggested a fit of this spectrum with 2-mercaptoethanol. If the procedure used to correct for the background was only slightly in error, this third component could be due to Me_2SO itself. When the base peak in the Me₂SO spectrum (at m/e 63) is removed during normalization and subtraction of background, the remaining peaks (at m/e 72, 47, and 15) are all spectral components in common with those of the unknown third species. Therefore, in the following discussion we have considered species 3 to be an uncorrected background component and have neglected it in our analysis of electrochemical products.

The production efficiencies for propionate oxidation, $P_{\rm CO_2}/i_0$ and $P_{C_2H_6}/i_0$ in Figure 6, do not vary in any systematic manner over an order-of-magnitude change in the current density. This observation is consistent with a single electrode reaction producing both products and with a conclusion that the current efficiency is virtually invariant for this process. The product ratio, $P_{C_2H_6}/P_{CO_2}$, shows slightly more variation, but there is still no systematic trend. Assuming that Kolbe

	ŗ	propionate produc	ets	a	cetate products	
i_0 , mA/cm ²	1	2	3	1	2	3
20	1.1	5.3	4.0	9.4	1.1	11.4
40	1.9	12.9	21.0	19.5	2.2	15.8
60	2.7	21.3	40.2	26.2	4.4	25.3
80	3.4	32.0	58.8	36.4	56	33.4
100	4.3	41.7	73.9	45.	6.8	39.7
120	5.2	49.7	86.1	55.3	7.5	46.6
140	6.2	58.3	99.3	62.5	8.1	52.4
160	$\bar{7.0}$	64.9	105	67.8	8.6	54.5
180	7.7	71.6	108	74.2	8.8	54.5
200	8.7	76.9	111	75.6	9.7	54.7
220	9.6	78.0	113	79.7	10.9	55.1
240	10.5	74.5	117	85.2	11.9	57.6
260	12.4	67.7	132	90.4	14.6	62.2
270				109	20.3	68.8
280	19.8	61.4	166	143	25.4	72.1
290			-	171	31.0	80.4
assigned	CO ₂	solvent	$C_{2}H_{6}$	solvent	CO_2	$C_{2}H_{2}$

C Matricies for Propionate and Acetate Oxidation in Me.SO Table VIII



Figure 6. Production efficiencies for Kolbe electrolysis at gold in Me₂SO medium: (X) CO₂ from propionate; (\bullet) C₂H₆ from propionate; (\otimes) CO₂ from acetate; (\overline{O}) C₂H₆ from acetate.

electrolysis of propionate produces CO_2 and C_2H_6 in equimolar quantities, the method shows approximately 20-fold greater sensitivity for ethane than for carbon dioxide.

Acetate oxidation shows similar behavior in Table VIII. $P_{\rm CO_2}/i_0$ and $P_{\rm C_2H_6}/i_0$ vary little from 20 to 260 mA/cm². However, the product ratio, $P_{C_2H_6}/P_{CO_2}$, is only about half the value observed for propionate. Because the experimental conditions were virtually identical for Kolbe electrolysis of propionate and acetate, these product ratios suggest that during acetate oxidation one molecule of ethane is produced for every two molecules of CO_2 . Obviously, this electroanalytical method can be useful in measuring yields of individual products as well as providing stoichiometric information on the reaction mechanism.

Diagnostic Application of the Method. Application of the PERMS method to characterization of an electrochemical reaction mechanism is based on the following range of measurements and analysis. A series of MS analyses of membrane-permeable products are taken during electrolysis at either controlled potential or controlled current. This set of mixed mass spectra is separated by factor analysis into spectra of individual components whose proportion vary with change in I_0 or E and an unresolved background spectrum. Finally quantitative comparison of product concentrations with current density yields information on current efficiency of

electrode reactions and information on production efficiency for individual species.

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Registry No. CO₂, 124-38-9; O₂, 7782-44-7; C₂H₆, 74-84-0; propionate, 72-03-7; acetate, 71-50-1.

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