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Coulometric Analysis with Gas Volume Measurement

SIR: A coulometric cell was designed and built which allows the measurement of volumes of gaseous electrolysis products. The cell is air-tight and the gas volume is determined by measuring the amount of water displaced in a graduated pipet by a technique similar to that used in gas coulometers (2). Provision was also made for withdrawing gas samples for analysis.

There are several applications of a cell allowing measurement of the amounts of gaseous products in coulometric determinations. If the electroactive species produces a gas on being oxidized or reduced, the amount of gas provides a simple way of obtaining material balance information about the reaction. Analysis of the gas can generally be easily done by mass spectrometry. Information about the kinetics of an electrode reaction can also be obtained. We have found this cell useful in studying the oxidation of hydrazine compounds, where nitrogen is not evolved in the initial electrode reaction, but by an intermediate, following chemical reaction. Some preliminary results are presented here on the oxidation of methyl hydrazines.

The most promising use of this cell is in the study of electrode reactions which occur at potentials sufficiently cathodic or anodic to cause concurrent oxidation or reduction of the solvent. Under these conditions, since the electrolysis does not proceed with 100% current efficiency, coulometric measurements cannot ordinarily be made. However, if the species of interest does not produce a gas upon electrolysis, the difference in coulombs obtained by current-time integration and those calculated from the volume of gas evolved during electrolysis of the solvent should give the total coulombs used in electrolyzing the species of interest. This use of the cell was tested by simultaneously reducing ferric and hydrogen ions at a platinum electrode.

EXPERIMENTAL

Cell and Apparatus. The cell is shown in Figure 1. The working electrode was platinum gauze, the reference electrode was a saturated calomel electrode (SCE) and the auxiliary electrode was a coil of platinum wire. The auxiliary electrode compartment was separated from the main compartment by a fine porosity sintered glass disk and an agar plug. Standard taper and ball joints were used throughout to make the cell gas-tight. The top cell joint was 34/28, the ball joints were 12/12, and the reference and working electrode inlets were 7/25. The seal around the wire leading to the
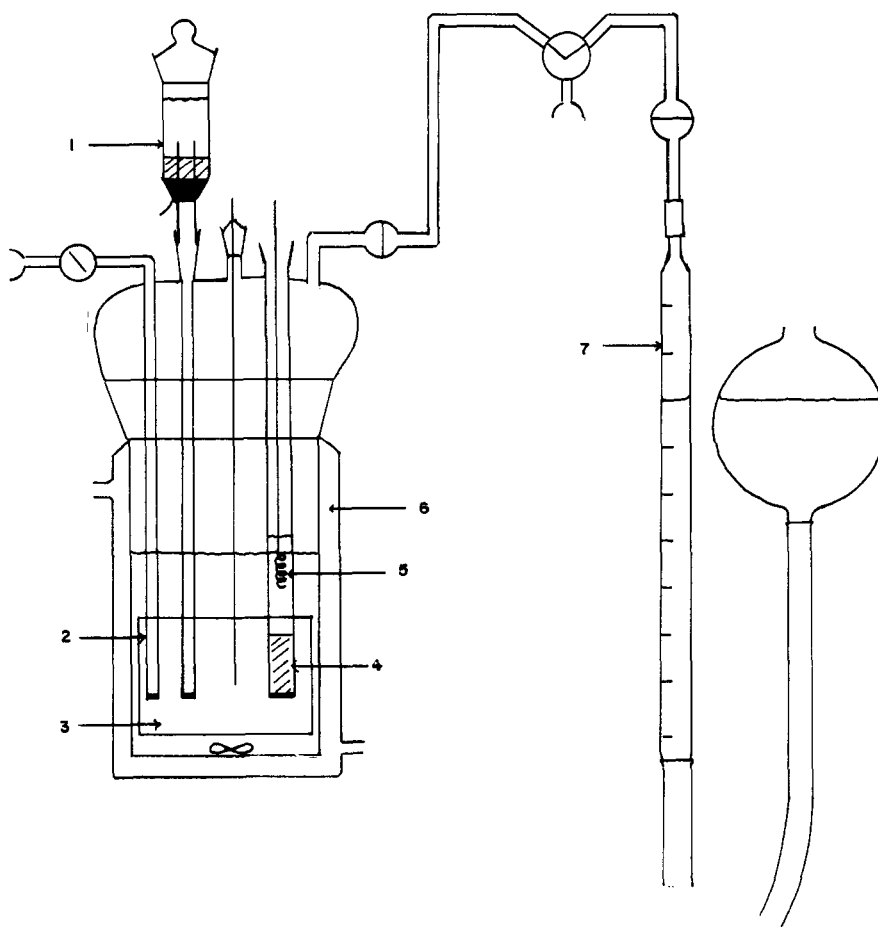

Figure 1. Electrolysis cell

1. Reference electrode. 2. Nitrogen inlet. 3. Platinum gauze electrode. 4. Agar plug. 5. Auxiliary electrode. 6. Cell jacket. 7. Gas pipet

working electrode was achieved with a weatherstrip adhesive (Minnesota Mining and Manufacturing Co., St. Paul, Minn.). The cell was jacketed and a magnetic stirrer was used. The three-way stopcock was used to direct the generated gas either to the measuring apparatus or to some collection apparatus. A 10 ml. pipet with an attached leveling bulb was used for volume measurement.

We have also used a cell with a rubber stopper top containing standard taper tubes for the reference and auxiliary electrode with equal success. The rubber stopper has the advantage of being simpler to construct and allowing the replacement of the auxiliary electrode chamber when the sintered glass disk becomes clogged. When a magnetic stirrer consisting of a powerful magnet held in the chuck of a stirring motor was employed and was positioned somewhat below the cell, heating of the solution by the stirrer did not occur, and the cell did not have to be

Table I. Coulometric Reduction of Iron(III) in Acidic Solution with and without Hydrogen Evolution

Solution: 25 ml. of 0.1M H_2SO_4. Electrolysis time; 10 to 15 minutes

Amount of iron(III) taken, meq.	E, volt vs. SCE	Vol. of gas, meq.	Coulometer rdg., meq.	Amount of iron(III) found, meq.
0.0	−0.4	0.560	0.568	
		0.554	0.558	
		0.619	0.617	
0.250	0.0	0.0	0.261	0.261
			0.245	0.245
	−0.4	0.237	0.473	0.236
		0.158	0.406	0.248
0.500		0.036	0.525	0.489

Table II. Coulometric Oxidation of Methyl Hydrazines

Solution: 1.0M in H_2SO_4. Oxidations carried out at +1.0 volt $vs.$ SCE

	Amount, mmol.	Coulometer rdg., meq.	n	Amount of nitrogen, mmol.
Methyl hydrazine	0.238	0.916	3.86	0.239
1,2-Dimethyl hydrazine	0.510	3.16	6.20	0.532
	0.239	1.42	5.94	0.240
1,1-Dimethyl hydrazine	0.326	1.53	4.7	0.194[a]
		1.92	5.9	0.270[b]

[a] Electrolysis interrupted for about 1 hour after 0.65 meq. oxidation.
[b] Electrolysis carried out continuously.

jacketed under stable laboratory temperature conditions.

An electromechanical potentiostat similar to that described by Lamphere and Rogers (1) was used. Current-time integration was accomplished with a ball-and-disk integrator attached to a strip-chart recorder.

Procedure. In the reduction studies, the solution in the cell was 0.1M in sulfuric acid and about 25 ml. in volume. Initial saturation with hydrogen was achieved by pre-electrolysis at about −0.4 volt $vs.$ SCE. Aliquots of standard iron(III) solution were then added and the electrolysis was performed. For the hydrazine oxidation studies the solution was 25 ml. of 1.0M H_2SO_4 and was presaturated with nitrogen.

RESULTS

Results for the electrolysis of ferric and hydrogen ions at various potentials are shown in Table I. When the electrolysis of iron(III) was carried out at 0.0 volt $vs.$ SCE, no hydrogen ion reduction occurred and the measured coulombs agreed with those calculated from the equivalent of iron added. Electrolysis at −0.4 volt leads to concomitant reduction of hydrogen ion; subtraction of the volume of hydrogen gas evolved, however, again allows calculation of the amount of iron.

Results for the oxidation of several methyl hydrazines are shown in Table II. Methyl hydrazine undergoes a four-electron oxidation and one mole of nitrogen is formed per mole of hydrazine. 1,2-Dimethyl hydrazine undergoes

a six-electron oxidation again with one mole of nitrogen formed per mole of hydrazine. The oxidation of 1,1-dimethyl hydrazine is complicated by slower intermediate chemical reactions. Quantitative nitrogen formation is not observed and the apparant n-value depends upon the rate at which the electrolysis is carried out. Further study of these systems will be reported elsewhere. In all cases the gaseous electrolysis product was identified by mass spectrometry as nitrogen.

The cell should also find use in constant current coulometry (coulometric titrations), especially for the production of strong oxidants and reductants. Adaption of the cell to electrolysis with a mercury electrode should be straightforward. Further work with this cell is in progress.

LITERATURE CITED

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Gasometric Analysis of Alkyl Azides with Sodium Iodide–Trichloroacetic Acid

SIR: Numerous good methods for the quantitative determination of azide ion are known. However, there are few methods for the determination of the covalently bound azido group. Ugi (10) has successfully adapted the reaction of aryl azide with arsenite ion (1–3) to the gasometric determination of the aryl azides.

$$ArN_3 + AsO_3^{-3} \xrightarrow{H_2O}$$
$$ArNH_2 + AsO_4^{-3} + N_2 \quad (1)$$
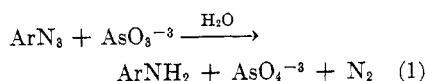
Messmer and Mlinko (6, 7) determined the azido group of 1-azido-1-acetyl sugars by ceric ion oxidation of hydrazoic acid liberated by acid digestion. However, except for certain azides, such as triphenylmethyl, acyl and sulfonyl azides, and the 1-azido-1-acetyl sugars, the azido group is not readily hydrolyzed intact by acid or base. The usual result of such attempts is cleavage

of the group to form nitrogen plus a complex mixture of imines, amines, olefins, keto compounds, etc. Hoffman, Hoch, and Kirmreuther (4) determined the azido group in guanyl azide and in carbamyl azide by measuring the nitrogen evolved in the reaction

$$RN_3 + 3HI \rightarrow RNH_3{}^+I^- + N_2 + I_2 \quad (2)$$
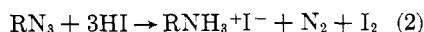
Water-insoluble azides were not investigated.

Smith (8) reported the reaction of aryl azides with hydroiodic acid to give iodine, nitrogen, and the corresponding arylamine. The determination of the azido group by titration of the liberated iodine was subject to error because of the tendency to form excess iodine by air oxidation of hydroiodic acid (9). The preparation and preservation of stock solutions of iodine-free hydroiodic acid constituted a further difficulty in this analytical approach. Leffler has

analyzed benzenesulfonyl azides by two methods (5). Reaction with triphenylphosphine caused quantitative liberation of nitrogen.

$$(C_6H_5)_3P + C_6H_5SO_2N_3 \rightarrow$$
$$C_6H_5SO_2\overset{-}{N} - \overset{+}{P}(C_6H_5)_3 + N_2 \quad (3)$$
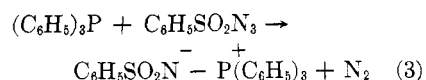
A potassium iodide–aqueous acetic acid combination brought about a quantitative liberation of iodine upon heating.

In this laboratory a method was sought for the analysis of various azides, primarily aliphatic. Ugi's (10) procedure was not suitable for simple alkyl azides because of their unreactivity with arsenite ion. Both of Leffler's methods were also unsuitable because of the poor reactivity of alkyl azides toward triphenylphosphine and potassium iodide–acetic acid. A method has been developed which is a modification of the hydroiodic acid reaction. It involves