

Chronopotentiometric Measurement of Adsorption by Current Reversal

SIR: The determination of the amount of an electroactive species adsorbed at an electrode is of current interest. The chronopotentiometric measurement of the amount of reactant adsorbed was described first by Lorenz (3); other work has recently been reviewed (6). Generally adsorption of the reactant causes $i_o\tau^{1/2}$ to increase as τ decreases. The extent of adsorption of the product of the electrode reaction can be studied by current reversal chronopotentiometry. Osteryoung (5) recently studied the iodide-iodine system by this technique and showed experimentally that when the product of the electrode reaction is adsorbed, the reverse transition time, τ_r , approaches the forward transition time, τ_f , in magnitude. This communication presents a theoretical model for the calculation of the extent of adsorption from current reversal chronopotentiometric

metric data, and gives results for the adsorption of iodine on platinum and leuco-riboflavin on mercury.

Various theoretical models for the process can be constructed, based upon assumptions concerning the relative formation and electrolysis of the adsorbed and the diffusing species, and different adsorption isotherms. A convenient model, especially useful for reversible electrode reactions, is based upon the concepts of Brdička (2). Although the following discussion will consider a reduction followed by a current reversal oxidation, where the reduced species is assumed to be adsorbed, the final results will hold equally well for an initial oxidation followed by a reduction. Brdička (2) has postulated that an adsorbed species is in a lower free energy state than a solution species, so that during the initial reduction the reduced species will first form an adsorbed monolayer, and then diffuse into the solution. Upon current reversal, the diffusing species will be oxidized first, and then the adsorbed monolayer. Therefore during the initial reduction, the flux of reduced product into the solution will be zero until time t_a , when the formation of the adsorbed monolayer is completed.

determined. The current density contributing to the oxidation of the adsorbed species, i_a , is then

$$i_a = i_o - i_d \quad (4)$$

The final reversal transition will occur when the adsorbed species is completely oxidized,

$$t_a' = \tau_r - t_d' \quad (5)$$

An equation for the amount of species adsorbed can be obtained by integration of $i_a dt$ from zero to t_a' , which yields

$$nF\Gamma = 2i_o \left[\frac{\tau_r}{\pi} \arccos \left(\frac{t_d' - t_a'}{\tau_r} \right) - \frac{2}{\pi} (t_d' t_a')^{1/2} \right] - i_o \left[\frac{(t_d + \tau_r)}{\pi} \arccos \left(\frac{t_d + t_d' - t_a'}{t_d + \tau_r} \right) - \frac{2}{\pi} \{(t_d + t_d') t_a'\}^{1/2} \right] \quad (6)$$

Calculation of Γ using the experimental values of i_o , τ_f , and τ_r , involves simultaneous solution of Equations 2, 3, 5, and 6.

A computer program was written which utilizes an iterative method for calculating Γ when different values of i_o , τ_f , and τ_r are read in. Using this program with current reversal chronopotentiometric data obtained during the reduction of riboflavin and the oxidation of iodide (5), Γ -values for adsorption of leuco-riboflavin and iodine were calculated (Table I). Data at long transition times are relatively insensitive to small amounts of adsorbed species, and were not included in the averages. The value of Γ for leuco-riboflavin is in good agreement with the value computed on the basis of molecular models, 0.2×10^{-9} mole per sq. cm. (6). The value for the adsorption of iodine, based on that found by Lorenz and Mühlberg (4), 0.5×10^{-9} mole per sq. cm., from the direct chronopotentiometric reduction of I_3^- . Using the atomic radius of iodine, 1.35 Å, and assuming the effective area of an iodine molecule to be 14.6 sq. Å, a monolayer containing a maximum of 1.1×10^{-9} mole per sq. cm. is calculated.

This model will hold rigorously only when a polarographic pre-wave is observed. When oxidation of the

Table I. Calculated Values of Γ from Current Reversal Data for Reduction of Riboflavin and Oxidation of Iodide Ion

A. RIBOFLAVIN. The solution contained 0.08mM riboflavin and 0.5M H_2SO_4 -1M Na_2SO_4 buffer. The mercury electrode area was 3.08 sq. cm. (6)

i_o , ma. per sq. cm.	τ_f , sec.	τ_r , sec.	Γ , $\times 10^9$ mole per sq. cm.
0.0413	40.4	15.8	0.15
0.0561	24.7	9.7	0.13
0.0811	10.9	5.0	0.26
0.114	6.0	2.8	0.22
0.189	3.0	1.6	0.34
0.233	1.8	1.0	0.30
0.316	1.2	0.70	0.36
0.454	0.80	0.50	0.40

$\Gamma_{avg.}$ (excluding first two measurements) is $0.31 \pm 0.07 \times 10^{-9}$ mole per sq. cm.

B. IODIDE ION. Data of Osteryoung (5). The solution contained 1mM iodide and 1M H_2SO_4 . The platinum electrode had an area of 1.6 sq. cm.

i_o , ma. per sq. cm.	τ_f , sec.	τ_r , sec.	Γ , $\times 10^9$ mole per sq. cm.
0.038	97	30	...
0.050	48	19	0.18
0.062	28	13	0.50
0.120	6.8	3.6	0.48
0.190	3.0	1.7	0.43
0.250	1.5	0.94	0.41
0.310	1.0	0.71	0.51

$\Gamma_{avg.}$ (excluding first two measurements) is $0.47 \pm 0.05 \times 10^{-9}$ mole per sq. cm.

$$t_a = nF\Gamma/i_o \quad (1)$$

where Γ is the amount of product adsorbed, and i_o is the current density. During the remainder of the forward transition time, t_a , reduced species diffuses into the solution.

$$t_d = \tau_f - nF\Gamma/i_o \quad (2)$$

On reversal of the current, the diffusing species reacts first, for a time t_d' , given by

$$t_d' = t_d/3 = (\tau_f - nF\Gamma/i_o)/3 \quad (3)$$

The adsorbed layer of reduced species is then oxidized. The current efficiency for this last process is less than 100%, however, because the reduced species in solution continues to diffuse to the electrode surface. The flux of the diffusing reduced species during this oxidation can be calculated by a procedure similar to that of Berzins and Delahay (1), and the current density at any time contributing to the oxidation of the diffusing species, i_d , can be

adsorbed product occurs simultaneously with oxidation of the diffusing species, calculations based on this model will give a value of Γ which is somewhat low. As in all cases of chronopotentiometric measurements of adsorption, the value of Γ obtained must be regarded as an estimate. A subsequent communication will further discuss the model presented here, as well as other models for current reversal chronopotentiometry.

LITERATURE CITED

- (1) Berzins, T., Delahay, P., *J. Am. Chem. Soc.* **75**, 4205 (1953).
- (2) Brdička, R., *Collection Czech. Chem. Commun.* **12**, 522 (1947).
- (3) Lorenz, W., *Z. Elektrochem.* **59**, 730 (1955).
- (4) Lorenz, W., Mühlberg, H., *Ibid.*, **59**, 736 (1955); *Z. Physik. Chem. Frankfurt* **17**, 129 (1958).
- (5) Osteryoung, R. A., *ANAL. CHEM.* **35**, 1100 (1963).

- (6) Tatwawadi, S. V., Bard, A. J., The University of Texas, Austin, Texas, unpublished data, 1963.

HARVEY B. HERMAN
SHANKAR V. TATWAWADI
ALLEN J. BARD

Department of Chemistry
The University of Texas
Austin 12, Texas

RECEIVED for review July 24, 1963.
Accepted September 23, 1963. Work supported by a grant of the Robert A. Welch Foundation.

Solvents for Phosphorimetry

SIR: The development of phosphorimetry as a means of analysis is highly dependent on the availability of solvents which form clear rigid glasses rather than cracked glasses or snows when cooled down to liquid nitrogen temperature. Phosphorimetry as a means of chemical analysis was introduced in 1957 by Keirs, Britt, and Wentworth (1). In 1962 a review by Parker and Hatchard (2) appeared. In 1963,

Winefordner and Latz (3) analyzed small concentrations of aspirin in blood with negligible interference and indicated that phosphorimetry could be applied to the quantitative analysis of trace concentrations of drugs in biological fluids. For the method of phosphorimetry to be used, suitable solvents must be readily available. Therefore, in this brief communication a large number of solvents which had

been previously described in the literature were studied in order to determine the number and kinds of solvents which will form clear rigid glasses at liquid nitrogen temperature.

In Tables I and II a large number of solvents and solvent mixtures, which had previously been purified by distillation, column chromatography over alumina, etc., are listed according to type and behavior on cooling down to

Table I. Behavior of Solvents upon Rapid Cooling with Liquid Nitrogen

Kind of solvent	Form of media at 77° K.	Frequency of forming cracks or snow	Possibility for use	Kind of solvent	Form of media at 77° K.	Frequency of forming cracks or snow	Possibility for use
Hydrocarbons				Di-isopropyl ether	Snow	10 out of 10	Not usable
Pentane (tech.)	Clear glass	0 out of 10	Excellent	1,4-Dioxane	Snow	10 out of 10	Not usable
Petroleum ether	Clear glass	1 out of 10	Good	Alkyl halides			
Heptane	Clear glass	9 out of 10	Not usable	Carbon			
Toluene	Clear glass	10 out of 10	Not usable	tetrachloride	Snow	10 out of 10	Not usable
Methyl cyclohexane	Clear glass	9 out of 10	Not usable	Chloroform	Snow	10 out of 10	Not usable
Iso-octane	Snow	10 out of 10	Not usable	Bromoform	Snow	10 out of 10	Not usable
Cyclohexane	Snow	10 out of 10	Not usable	Dichloromethane	Snow	10 out of 10	Not usable
Benzene	Snow	10 out of 10	Not usable	Tetrachloroethylene	Snow	10 out of 10	Not usable
m-Xylene	Snow	10 out of 10	Not usable	1-Bromopropane	Snow	10 out of 10	Not usable
Hexane	Snow	10 out of 10	Not usable	2-Chloropropane	Snow	10 out of 10	Not usable
Bases and N-containing Compounds				1,2-Dibromo-ethylene	Snow	10 out of 10	Not usable
Triethylamine	Clear glass	5 out of 10	Poor	2-Bromobutane	Cloudy glass	2 out of 10	Good
Triethanolamine	Clear glass	10 out of 10	Not usable	2-Bromopentane	Snow	10 out of 10	Not usable
Dimethyl formamide	Glass or snow	10 out of 10	Not usable	Alcohols			
Isopropylamine	Clear glass	10 out of 10	Not usable	Methanol	Clear glass	10 out of 10	Not usable
Pyridine	Snow	10 out of 10	Not usable	Ethanol	Clear glass	1 out of 10	Good
Diethylamine	Snow	10 out of 10	Not usable	n-Propanol	Clear glass	2 out of 10	Good
Dipropylamine	Snow	10 out of 10	Not usable	Isopropanol	Clear glass	9 out of 10	Not usable
Formamide	Snow	10 out of 10	Not usable	n-Butanol	Clear glass	4 out of 10	Poor
N,N-dimethyl-formamide	Snow	10 out of 10	Not usable	Isobutanol	Clear glass	10 out of 10	Not usable
Acetonitrile	Snow	10 out of 10	Not usable	4-Chloro-1-butanol	Clear glass	10 out of 10	Not usable
Ethers				Isoamyl alcohol	Clear glass	8 out of 10	Poor
Diethyl ether	Clear glass	1 out of 10	Good	Glycerol	Clear glass	10 out of 10	Not usable
Di-n-propyl ether	Clear glass	9 out of 10	Not usable	Ethylene glycol	Snow	10 out of 10	Not usable
Di-n-butyl ether	Clear glass	9 out of 10	Not usable	Miscellaneous			
Methyl cellosolve	Clear glass	10 out of 10	Not usable	Acetone	Snow	10 out of 10	Not usable
Ethyl cellosolve	Clear glass	10 out of 10	Not usable	Methyl isobutyl ketone	Snow	10 out of 10	Not usable
Butyl cellosolve	Clear glass	10 out of 10	Not usable	Acetic acid	Snow	10 out of 10	Not usable
Dimethoxymethane	Snow	10 out of 10	Not usable	Formic acid	Snow	10 out of 10	Not usable
Ethyl cellosolve acetate	Snow	10 out of 10	Not usable	Perfluorocarbon oil (Kel F)	Snow	10 out of 10	Not usable