of the cation across the chloroform membrane in the blank unit. A plot of moles of cation transported vs. time was made for each system studied, the slope of which indicates rate of transfer. Such plots were invariably linear as in similar experiments by other workers,[2,4] and deviation in slopes between different runs of the same system was <10%.

Table I lists the cation transfer rates in moles of cation which move across the chloroform membrane per hour for the various salts of the four cations studied. These rates of transfer can be compared only by normalizing all initial solution concentrations to the same value. From the transfer rate of KI at various concentrations, we find that transfer rate varies essentially linearly with the concentration of the originating solution over the range of concentrations studied. This relationship was used to adjust transfer rates of KBF_4, KPF_6, K picrate, and $KClO_4$ to those of 1 M solutions. This method of adjustment is probably conservative as the rates for KI at higher concentrations are actually somewhat higher than a straight-line extrapolation from lower concentrations would predict.

The ordering of anions according to transfer rate is consistent with size–charge considerations which would be expected to determine the ion's affinity for a polar solvent like water and commensurate lack of affinity for chloroform. For instance, among the halides, it is true for every cation–carrier combination that the iodide always transfers most rapidly, followed in order by the bromide, chloride, and fluoride. The large monopositive anions like picrate, PF_6^-, ClO_4^-, $H_2PO_4^-$, NO_3^-, and BF_4^- transfer more rapidly than the smaller ones such as OH^- and the smaller halides. In addition, the multiply charged phosphates transfer little if at all. These results suggest that the anion desolvation energy barrier is one of the more important factors in controlling the rate of transfer across the membrane.

No attempt was made to buffer solutions of weak acid salts and undoubtedly hydrolysis was influential in such cases. This may partially account for picrate having a higher transfer rate than benzoate and the anomalously low transfer rate of acetate. This pH effect will also play a significant role in the case of the mono-, di-, and trivalent phosphates.

To check the findings of Kobuke et al.[7] who used mixtures of K picrate and KNO_3 in experiments similar to ours and who measured K^+ concentrations via picrate determination only, we measured the transfer rate for K^+ carried by dibenzo-18-crown-6 with both anions present. Transfer samples were analyzed for K^+ via atomic absorption and for picrate ion via colorimetry. No measurable difference could be detected between the rate of transfer of K^+ and that of picrate. Thus it appears that, when more than one anion is available for cotransport, the anion which normally transfers more readily will be preferred over the other.

The barium salts gave lower transfer rates than would be expected from the fact that Ba^{2+} normally binds to crown-6 ligands as well as or better than K^+.[5] The energy expended in desolvating a dipositive ion along with two monopositive anions must be prohibitive.

The magnitude of the effect of anion on the facilitated transport of cations across liquid membranes holds significant implications. Comparisons of transport carrier effectiveness and system design can only be made where a common anion has been employed. Furthermore, the anion effect may be exploited in that transport of cations across membranes can be turned on or off simply by altering the anion present in the source solution. This same anion effect might be useful in separating or detecting anions themselves.

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J. J. Christensen,* J. D. Lamb, S. R. Izatt
S. E. Starr, G. C. Weed, M. S. Astin, B. D. Stitt, R. M. Izatt

Contribution No. 138
Departments of Chemistry and Chemical Engineering
and the Thermochemical Institute
Brigham Young University, Provo, Utah 84602
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Electrochemistry of Vitamin B_{12}. 3. One-Electron Intermediates in the Reduction of Methylcobalamin and Methylcobinamide

Sir:

Although redox processes are likely to be involved in the enzymic reactions of methylcobalamin,[1] there have been much less studies on the electrochemistry[2-4] of this biologically important compound, than, e.g., on its photochemical behavior (see ref 5 and references therein). Investigations in the related field of γ-ray radiolysis have concerned cyanocobalamin and 5'-deoxyadenosylcobalamin[6,7] but not methylcobalamin. The previous electrochemical studies have given indications on the number, height, and potential location of the polarographic[2,4] and cyclic voltammetry[3] waves in water[2,3] and DMF[4] of methylcobalamin[2-4] and methylcobinamide.[2,3] However, these data are most probably affected by absorption on mercury.[3] On the other hand, attempts to detect a one-electron intermediate before cleavage of cobalt–carbon bond have been unsuccessful so far.[4]

We report here on the results of a preliminary investigation of the electrochemical reduction of methylcobalamin and cobinamide showing the existence of such one-electron intermediates. Estimations of the lifetime of the intermediates and of the standard potentials of the electrontransfer processes were also obtained.

In water, reactant adsorption seriously affects the polarization curves of both compounds. Some reversibility is observed upon raising the sweep rate. It could be, however, related to adsorption on mercury. Addition of a salt of a large organic cation such as tetrabutylammonium tends to decrease adsorption as in the case of the B_{12r}/B_{12s} system,[8] but the reduction wave is then too close to the proton or supporting electrolyte discharge, especially in the case of methylcobalamin, to allow the analysis of the reduction process. Mixtures of DMF with water or, better, with ethanol or 1-propanol were found suitable for our purposes. Separation between the reduction wave and the supporting electrolyte was satisfactory. Adsorption effects on the alkylcobalt reduction waves were practically absent as checked by comparison with results obtained with a gold or vitreous carbon disk electrode. Some interference of adsorption was however still noticeable at the B_{12s}/B_{12r} wave obtained upon scan reversal at low sweep rates (Figure 1).

Methylcobinamide shows a simpler behavior than methylcobalamin owing to the absence of the nucleotide side chain. At -20 °C (Figure 1) a single irreversible cathodic wave was observed at low sweep rates corresponding to the reductive cleavage of the cobalt–carbon bond. A reoxidation wave indeed appears upon scan reversal in the same potential region (-0.75 V vs. SCE) as the oxidation of cob(I)inamide.[9,10] Upon raising the sweep rate the cathodic wave becomes progressively reversible, clearly showing the existence of a one-electron in-
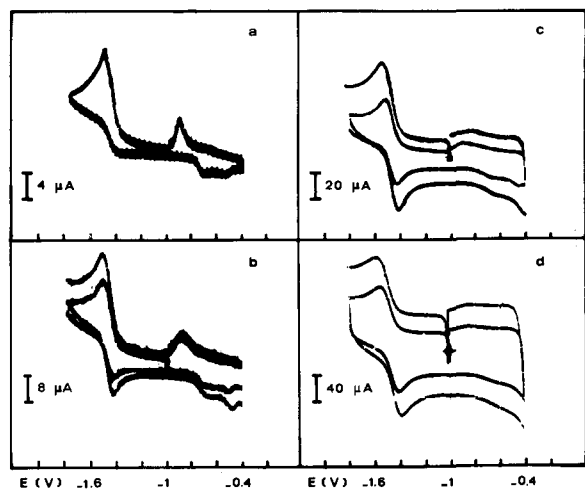
Figure 1. Cyclic voltammetry of methylcobinamid at −20 °C in 1:1 DMF-1-propanol: supporting electrolyte, NBu₄BF₄ (0.2 M); reference electrode, aqueous SCE; potential scanning, −1 → −1.8 → −0.4 → −1 V; sweep rate (V s⁻¹), (a) 1, (b) 5, 10, (c) 20, 50, (d) 100, 200.

Figure 2. Cyclic voltammetry of methylcobalamin at −20 °C in 1:1 DMF-1-propanol: supporting electrolyte, NBu₄BF₄ (0.1 M); reference electrode, aqueous SCE; potential scanning, (a, b) −0.5 → −1.9 → −0.5; (c, d) −0.5 → −1.85 → −0.5 V; sweep rate (V s⁻¹), (a) 2, 5, (b) 10, 20, (c) 20, 50, (d) 100, 200.

termediate before cleavage of the cobalt–carbon bond. Concomittantly, the Co(I) reoxidation wave disappears and the $i_p/\sqrt{v}$ ratio of the cathodic wave passes approximately from 2 to 1 suggesting that the irreversible process occurring at slow sweep rate involves the overall exchange of two faradays per mole. Complete reversibility is practically reached at 200 V s⁻¹. Similar results were obtained at other temperatures ranging from −20 °C to 20 °C. As expected the value of the sweep rate at which complete reversibility is observed increases with temperature. Estimation of the rate constant[11] of the CH₃ cleavage in the one-electron intermediate and of the standard potential of methylcobinamide reduction led to the following results:

| Temp, °C	−20	−11	0	19
Rate constant, s⁻¹	14	50	180	2500
$E°$ (V vs. aqueous SCE)	−1.47	−1.47	−1.46	−1.46

An Arrhenius plot treatment of the rate constant results leads to 19 kcal mol⁻¹ as activation energy and $\log A = 17.6$ (A in s⁻¹) as pre-exponential factor.

When compared with model compounds, the one-electron intermediate appears as markedly more unstable toward methyl cleavage. Indeed for, e.g., CH₃CoSalen in DMF, the system is almost reversible at 25 V s⁻¹ at room temperature;[12] with methylcobalttetraphenylporphin[13] in DMF complete reversibility is even reached for sweep rates as small as 0.1 V s⁻¹ at 20 °C. This difference in stability is not likely to be due to the interference of corrin ring protons or hydrogen atoms as previously hypothesized[4] since CH₃ radicals are essentially scavenged by the solvent in the case of DMF and alcohols which are good H-atom donors.[14] It should rather be related to different cis electronic effects.

Methylcobalamin shows a similar behavior in cyclic voltammetry (Figure 2). There is, however, a significant difference: the increase of reversibility upon raising the sweep rate involves the appearance of two anodic waves instead of one, the most positive being located in the same potential region as the reoxidation of the one-electron intermediate of methylcobinamide. These two waves, with the same potential location, are also observed on gold, showing that none of them arises from remaining adsorption on mercury.

Upon raising the sweep rate the two anodic waves first separate and then the less anodic wave increases at the expense of the second one. Very high sweep rates are required to obtain complete disappearence of the most anodic reoxidation waves (3500 V s⁻¹ at −30 °C). This suggests the reaction shown in
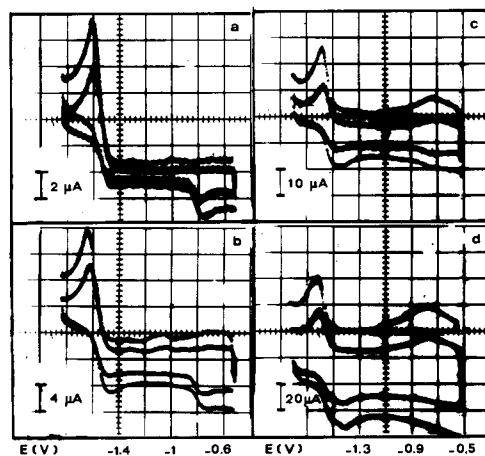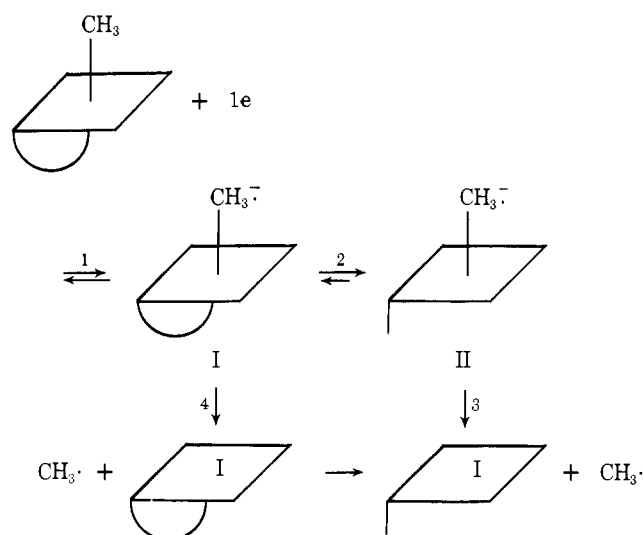
Scheme I

Scheme I for the reduction of methylcobalamin with the less anodic reoxidation wave corresponding to reoxidation of I and the other one to reoxidation of II. The rate constant for the disappearance of I through reaction 2 and 4 was estimated[11] as 1200 s⁻¹ at −30 °C and the standard potential of electron transfer (1) as −1.60 V (vs. aqueous SCE) at the same temperature.

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Doris Lexa

Laboratoire de Biophysique du Muséum National
d'Histoire Naturelle, 61, Rue Buffon
75005 Paris, France

Jean-Michel Savéant*

Laboratoire d'Electrochimie de l'Université de Paris VII
75221 Paris, Cedex 05, France

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Figure 1. Cyclic voltammograms of polyvinylferrocene at a 0.07-cm^2 platinum disk (scan rate, 200 mV/s): (a) 10^{-5} M solution in CH_2Cl_2/0.1 M TBAP; (b) coated on the same electrode in acetonitrile/0.1 M TBAP; —, first cycle; ⋯, 250th cycle.

A Stable Surface Modified Platinum Electrode Prepared by Coating with Electroactive Polymer

Sir:

Recent studies have demonstrated that solutions of polymers containing noninteracting electroactive centers along the polymer chain in some aprotic solvents show multielectron voltammetric waves with the same wave shape as anticipated for reversible one-electron oxidation/reduction reactions.[1] While in some solvents the polymers show ideal cyclic voltammetric behavior characteristic of both reduced and oxidized forms being dissolved, in many solvent-supporting electrolyte systems the cyclic voltammograms showed sharp surface peaks apparently caused by strong adsorption or precipitation of either the reduced or oxidized form of the polymer on the electrode surface. In a solvent in which both the oxidized and reduced forms of a polymer are insoluble or strongly adsorbed on the electrode, the electrode should closely resemble a chemically modified electrode, several types of which have been recently described (see ref 2–8 and references therein). We report here the preparation of polyvinylferrocene (PVF)-coated platinum electrodes and their electrochemical behavior in acetonitrile (ACN) solutions. The PVF used had an average molecular weight of 15 750, corresponding to a degree of polymerization of 74.3 and the electrochemical behavior of solutions of PVF has been previously described.[1b,9]

In a typical experiment, a clean, polished 0.07-cm^2 platinum disk surface sealed in soft glass was coated from an $\sim 10^{-5}$ M solution of PVF in dichloromethane containing 0.1 M tetra-*n*-butylammonium perchlorate (TBAP). The cyclic voltammogram of this system (Figure 1a) was similar to that found in THF[1b] and consisted of a broad anodic peak at +0.30 V and, on reversal, a sharp cathodic peak at +0.13 V (vs. a silver wire pseudo reference electrode),[10] indicating adsorption or precipitation of the oxidized polymer. Continuous cyclic scans of the potential between −0.3 and +0.7 V resulted in an increase in the heights of both peaks to give a steady-state voltammogram with an integrated peak current of 570 $\mu C/cm^2$ or 0.80 × 10^{-8} Faradays/cm^2. The working electrode was held at a potential of +0.7 V for a period of 2 min and was removed from the dichloromethane solution, and the adherent excess solution was removed immediately with a soft tissue. Upon immersion into an ACN solution containing 0.1 M TBAP, this pretreated electrode gave a cyclic voltammogram with sharp anodic and cathodic peaks at +0.365 and +0.345 V, respectively (Figure 1b). The peak shapes (with a half-height width of $\sim$80 mV at a scan rate of 20 mV/s) as well as the integrated peak areas (1.2 ($\pm$0.2) × 10^{-8} Faradays/cm^2 at scan rates $\leq$200 mV/s) were very reproducible for different trials. The results were essentially the same for a platinum disk sealed in glass elec-
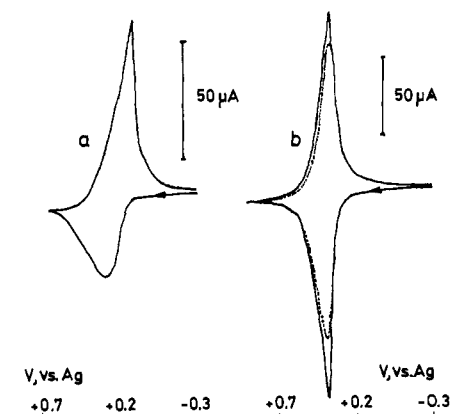
trode or a platinum wire electrode positioned with the wire-glass seal out of contact with the solution. This latter experiment shows that the observed results do not arise from trapping of solution in microscopic cracks at the platinum-glass seal giving rise to "thin layer effects".[11]

With slow scan rates ($\leq$0.2 V/s) the peak-to-peak separation, ΔE_p, remained nearly constant at values of 20 mV or less and the peak currents, i_{pc} and i_{pa}, were directly proportional to the scan rate, v, consistent with the confinement of both oxidized and reduced forms to the electrode surface.[12] However, the cathodic peak, at these scan rates, was somewhat broader than the anodic peak, so that i_{pc}/i_{pa} was 0.6 to 0.8, although the integrated currents of both peaks were equal. At higher scan rates ΔE_p increased to 400 mV at 100 V/s, symmetrically with respect to the original peak-to-peak center, while the peak current ratio i_{pc}/i_{pa} approached unity and the integrated peak current dropped to $\sim$20% of its value at low scan rates.

If we assume, as found in solution studies,[1b] that the number of electrons transferred per molecule of PVF is the same as the degree of polymerization, and that the PVF is distributed uniformly on the Pt surface, then the integrated peak area at slow scans corresponds to $\sim$2.1 μg of PVF/cm^2. Assuming a density of $\sim$1 g/cm^3 for the polymer, this represents a film thickness of $\sim$210 Å. This corresponds to a layer containing at least 20 (and probably more) monolayers of individual ferrocene units. The decrease in peak area observed with increasing v could represent electron-transfer rate limitations to outer portions of the film.

The PVF-coated electrode in many respects resembles the Pt electrode modified by chemically bound silylferrocene recently described by Wrighton and coworkers.[13] It is very durable. After standing in ACN solution for 24 h, the electrode behavior was practically unchanged; when repeated cyclic voltammograms were taken between −0.3 and +0.7 V, only a 12% drop of the integrated peak current was observed after 250 cycles at 200 mV/s (Figure 1b). A total potential range of −3.0 to +1.5 V (vs. Ag) could be scanned without affecting the electrochemical behavior of the coating. Extension of the scan to potentials beyond these limits, even for very short times, caused peak broadening and separation and, after a few repeated scans, total disappearance of the polymer peak into the background. Similar stable, but less reproducible, coatings were obtained by simply dipping a Pt electrode into a PVF solution of CH_2Cl_2, wiping off the excess solution, and drying in air.

Two substrates, diphenylanthracene (DPA) and anthraquinone (AQ), were chosen to study the behavior of dissolved