respectively, involve atoms of the axial ligand. No contacts, however, are less than 3.50 Å.

A thermodynamic study[16] of the formation of the five-coordinate cobalt complexes has been interpreted as indicating M → Lπ* back-bonding when the axial ligand is an aromatic amine. Furthermore, imidazoles were found to form more stable complexes than pyridines of the same σ-donor strength,[16] suggesting that imidazoles are better π acceptors than the pyridines. Possible π back-bonding for the imidazole complexes is also suggested by their reluctance to add a second ligand; the addition of a second imidazole would require substantially lengthened Co–Nb bonds and, hence, decrease the π-accepting ability of the imidazole. The Co–Nb bond length of MImCoTPP is compatible with π back-bonding but certainly cannot be regarded as compelling evidence for such bonding. Since imidazoles do not have significant π acceptor capacity in the low-spin bis(imidazole)ferrous and -ferric porphyrins,[17] the possible π-acceptor ability in the five-

coordinate porphyrins must be related to the displacement of the cobalt out of the porphyrin plane.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24X reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $4.00 for photocopy or $2.00 for microfiche, referring to code number JACS-74-90.

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Kinetics and Mechanism of Alkylchromium Formation in the Reductive Cobalt–Carbon Bond Cleavage of Alkylcorrins by Chromium(II)[1]

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Abstract: The stoichiometry and kinetics of reactions of methyl and ethylcobalamin with Cr^{2+} in aqueous perchloric acid have been examined. These reactions occur with a 1:1 stoichiometry, producing $(H_2O)_5CrCH_3^{2+}$ and $(H_2O)_5CrC_2H_5^{2+}$ (respectively), and B_{12r}. The reactions follow second-order kinetics, the rate constants (298°K, $\mu \sim 1\ M$) being $3.6 \pm 0.3 \times 10^2$ and $4.4 \pm 0.4\ M^{-1}$ sec^{-1}. In the same medium B_{12a} is reduced by Cr^{2+} at a specific rate of $14.3 \pm 1.0\ M^{-1}$ sec^{-1}. The reactions show no dependence upon pH in the range 0–2.3. Activation parameters were determined. Two plausible mechanisms are proposed, one of which is a direct bimolecular homolytic attack (SH2) at the saturated carbon center.

Treatment of organocobalt complexes with reducing agents under appropriate conditions results in cleavage of the Co–C bond. Thus Schrauzer and co-workers have realized the reductive cleavage of alkylcorrins and of related model compounds by thiols,[2] and by alkaline CO, $S_2O_4^{2-}$, and Sn(II).[3] These reactions result in the effective transfer of a carbanion, the products being the Co^I(chelate) or a compound derived therefrom, and the alkane. Reactions with electrophilic reagents such as Hg^{2+} and Tl^{3+} also result in carbanion transfer but no reduction; HgR$^+$, for example, is formed along with $(H_2O)_2Co^{III}$(chelate).[4–8]

Recently, two reactions were reported in which reductive cleavage of the Co–C bond resulted in transfer of an alkyl radical. The first of these was the reaction of a methylcobalt(III) (chelate) complex with a Co(II) derivative of a different chelate

$$CH_3Co(L) + Co^{II}(L') \rightleftharpoons Co^{II}(L) + CH_3Co(L') \qquad (1)$$

where L and L′ represent the two different planar, tetradentate, Schiff's base chelates.[9] The second reaction was that between alkylaquobis(dimethylglyoximato)cobalt(III) complexes (alkylcobaloximes) and Cr^{2+} in aqueous solution[10]

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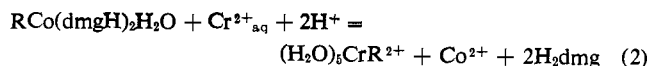
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$RCo(dmgH)_2H_2O + Cr^{2+}_{aq} + 2H^+ =$

$$(H_2O)_5CrR^{2+} + Co^{2+} + 2H_2dmg \quad (2)$$

We have now extended work in this area to include a study of the reactions of the corrin complexes themselves and report here on the stoichiometry and kinetics of the reactions of methylcobalamin and ethylcobalamin with Cr^{2+} in aqueous solutions of perchloric acid–lithium perchlorate.

Results

Products and Stoichiometry. The reactions occur according to the equation

$$RCo(corrin) + Cr^{2+}_{aq} \longrightarrow (H_2O)_5CrR^{2+} + B_{12r} \quad (3)$$
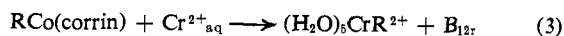
where B_{12r} represents aquo[cobalamin(BzmH+)]cobalt-(II). The stoichiometry was established by spectrophotometric titration. Plots of absorbance vs. the ratio of the added quantities of Cr^{2+} and alkylcobalamin are shown for the methyl derivative in Figure 1. Breaks were noted at a 1:1 ratio, in support of eq 3.

The spectrum of the Co(II) reaction product was identical with that reported for B_{12r}[11] and with a sample of B_{12r} prepared here by reduction of aquocobalamin (B_{12a}) with amalgamated zinc in the same medium.

Confirmation that the product is $CrCH_3^{2+}$ was obtained by several independent tests. Upon completion of reaction 3, a further slow decrease in absorbance was noted at wavelengths corresponding to peak maxima for $CrCH_3^{2+}$.[10,12,13] Both the magnitudes of the absorbance changes and the apparent rate constant $(k_{obsd}/[H^+] = 4.8 \pm 0.6 \times 10^{-3} M^{-1} sec^{-1}$ at 25° over a range $0.13 < [H^+] < 1.1 M)$ agreed with the known values for the acidolysis of the methylchromium cation

$$(H_2O)_5CrCH_3^{2+} + H_3O^+ = Cr(H_2O)_6^{3+} + CH_4 \quad (4)$$
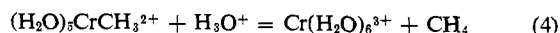
for which the reported rate constant is $5.2 \times 10^{-3} M^{-1} sec^{-1}$.[12] Subtracting the spectrum of B_{12r} from that observed immediately upon completion of reaction 3 generated a difference spectrum, with considerable inaccuracy, however, which matched that of the authentic methylchromium cation reasonably well.[10,12,13] Mass spectral analyses of the volatile products showed only methane peaks, consistent with eq 4. Product solutions also were treated with $Br_2(aq)$, both immediately after reaction 3 was complete as well as at much longer times corresponding to complete acidolysis of the methylchromium cation. The former samples had a mass spectrum corresponding to methyl bromide, known to be formed in the reaction of methylchromium with aqueous bromine[14]

$$(H_2O)_5CrCH_3^{2+} + Br_2 + H_2O = Cr(H_2O)_6^{3+} + Br^- + CH_3Br \quad (5)$$
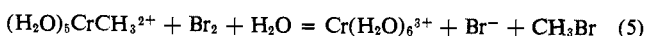
The solution aged before bromine addition gave no detectable CH_3Br in the mass spectrum, consistent with prior destruction of $CrCH_3^{2+}$ in reaction 4.

In the case of $CrC_2H_5^{2+}$ the reaction solution was passed through a short column of XAD-4 macroreticular resin. The cobalamins are retained on the resin, and the chromium product passes through along with the

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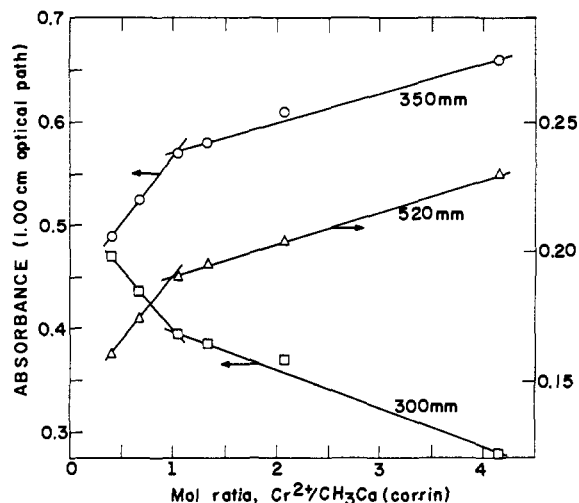(14) J. H. Espenson and D. A. Williams, submitted for publication.

Figure 1. Spectrophotometric titrations of $2.8 \times 10^{-6} M$ methylcobalamin with Cr^{2+} at three different wavelengths.

Cr(III) products from the oxidation of the excess Cr^{2+}. The product spectrum[15] agrees well with that of authentic $CrC_2H_5^{2+}$, as does the apparent rate of acidolysis[16] and the mass spectral data.

Kinetics. Excesses of Cr(II) were employed in the rate experiments, such that $[Cr^{2+}]$ remained essentially constant in any experiment. The kinetic data were consistent with a pseudo-first-order dependence upon the concentration of the cobalamin, in that the rate plots were linear and at a given $[Cr^{2+}]$ the rate was independent of the concentration of the cobalamin.

A few measurements were made with aquocobalamin, which reacts with Cr^{2+} according to

$$(H_2O)_2Co(corr)^+ + Cr^{2+} \longrightarrow B_{12r} + Cr^{3+} \quad (6)$$
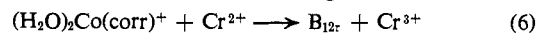
$$-d[B_{12a}]/dt = k[B_{12a}][Cr^{2+}] \quad (7)$$

with $k = 14.3 \pm 1.0 M^{-1} sec^{-1}$ at $25.0°$, $0.06 < [H^+] < 1.2 M$, at $\mu = 1.0$–$1.2 M$.

Chromatography of the methylcobalamin samples on XAD-4 indicated the presence of *ca.* 1% B_{12a}. In the kinetic runs with methylcobalamin and Cr^{2+}, this small amount of B_{12a} gave rise to a much slower secondary absorbance change; the latter corresponded simply to reaction 6, and could be enhanced further by deliberate addition of B_{12a}. The rate was so much slower than that of methylcobalamin, however, that it did not interfere in the kinetic determinations.

The range of $[CH_3Co(corr)]$ was 7.3×10^{-6}–$4.8 \times 10^{-5} M$ and of $[C_2H_5Co(corr)]$ 3.3–$5.3 \times 10^{-5} M$. In each case an attempt was made to cover a wide range of $[Cr^{2+}]$, as the question of this rate dependence is critical to the consideration of mechanism.

The pseudo-first-order rate constants at $25.0°$ are plotted against $[Cr^{2+}]$ in Figure 2; the linearity and zero intercept are consistent with the rate law

$$-d[RCo(corr)]/dt = k_R[RCo(corr)][Cr^{2+}] \quad (8)$$

(15) The product thus separated has absorption maxima at λ 380 nm (ϵ 350 M^{-1} cm^{-1}) and 275 (1600) compared to values found in two alternative syntheses of $CrC_2H_5^{2+}$, with maxima at 394 nm (ϵ 260) and 275 (1600).

(16) The pseudo-first-order rate constant for acidolysis was 3.0×10^{-4} sec^{-1} ($25.0°$, $[H^+] = 0.9 M$), compared to 3.0×10^{-4} sec^{-1} on authentic samples with $[H^+] = 1.0 M$. The reaction was followed at λ 275 nm, and the absorbance change in a 5-cm cell was 0.452. The expected absorbance decrease was 0.533 based on the initial concentration of ethylcobalamin assuming a 100% yield of the ethylchromium cation and quantitative recovery in the separation.
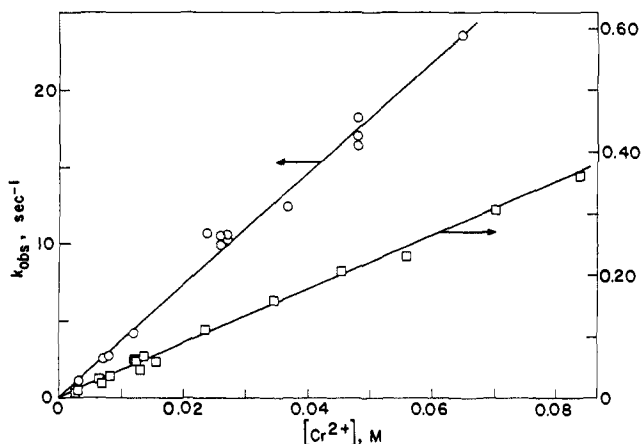
Figure 2. Plots showing the first-order rate dependences upon $[Cr^{2+}]$ of the reactions of alkylcobalamins: upper curve, Me; lower curve, Et.

Figure 3. Plots of $\ln(k/T)$ vs. $1/T$ for the reaction of alkylcobalimins with Cr^{2+}.

with $k_{Me} = 3.57 \pm 0.30 \times 10^2$ and $k_{Et} = 4.40 \pm 0.35$ M^{-1} sec^{-1}. Included on these plots are experiments covering a range of $[H^+]$, 2.5×10^{-3}–1.2 M for methylcobalamin and 5×10^{-3}–1.2 M for the ethyl derivative; $[H^+]$ variation is seen to have no effect on the rate constants. The ionic strength was maintained in these experiments between 1.0 and 1.2 M by addition of lithium perchlorate. An independent series of experiments showed that variation of lithium perchlorate concentration at $[H^+] = 0.09$ to provide ionic strengths between 0.8 and 1.45 M had no rate effect. The lack of a noticeable salt effect over a modest range of ionic strengths is the expected result for eq 8 in which one of the reactants is an uncharged molecule.

Rate measurements were carried out between 4.4 and 34.4° for the methylcobalamin and between 1 and 34.1° for the ethyl derivative (see Figure 3). Activation parameters are $\Delta H_{Me}^{\ddagger} = 15.9 \pm 0.9$ kJ mol^{-1}, $\Delta S_{Me}^{\ddagger}$ $= -144 \pm 4$ J mol^{-1} K^{-1} and $\Delta H_{Et}^{\ddagger} = 46.5 \pm 2.1$, $\Delta S_{Et}^{\ddagger} = -77 \pm 8$.

Interpretation and Discussion

Alkylcobalamins in acidic aqueous solution are subject to equilibria between species in which benzimidazole is coordinated and in which it is protonated and not coordinated.[17] The latter species include forms in which water occupies a sixth coordination position and in which it does not. This protonation equilibrium in the case of the Et derivative is characterized by a pK_a value of 3.87.[18] Consequently in the pH range 0–2.3 of the present study, the proportion of coordinated benzimidazole is quite small. The corresponding constant for the Me derivative is 2.72,[19] which suggests that in the pH range of interest here, 0–2.6, the predominant species is the one in which benzimidazole is protonated. Nevertheless the rate here also shows no pH dependence, so that either the two forms have comparable reactivity or (more likely) the values are not sufficiently accurate to detect a difference in rate. An attempt was made to check this point by studies at
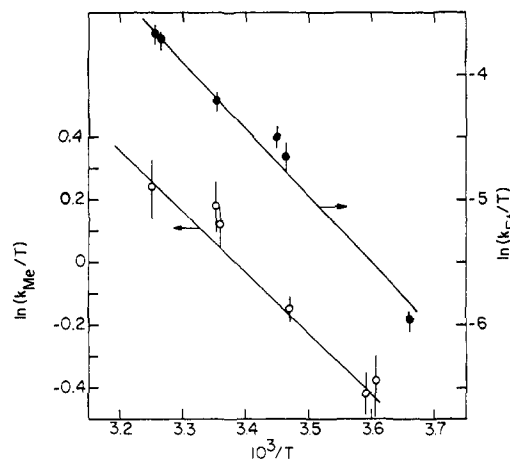
higher pH, where a larger proportion of methylcobalamin should not be protonated, but the Cr^{2+} solutions were not sufficiently stable.

The major pathway thus appears to be a bimolecular reaction between Cr^{2+} and $RCo(corrBzmH^+)$; it is not known if the reactive cobalamin species is the five-coordinate species or that with a water molecule trans to the alkyl group. The reaction mechanism appears to consist of an SH2 displacement at the saturated carbon, which is a rather uncommon process.[20-22] We must consider also the possibility of a different bimolecular mechanism in which a Co(III)–Co(II) redox process is accompanied or followed by transfer of a carbanion to the coordination sphere of Cr(III) (a "redox SE2" sequence). These possibilities are only subtly different and we cannot as yet resolve this question. We note that the decrease in rate of ca. 10^2 on going from Me to Et is in the same order as the reduction potentials which show that the methyl derivative, at least in model compounds, is the better oxidizing agent.[23] On the other hand, were carbanion character first developed at the alkyl in a redox process, the evolution of the alkane by reaction with H^+ should compete well with the reaction of the carbanion with the newly formed Cr(III).[2,3] This does not occur. Furthermore, to result in quantitative transfer of the alkyl group would require an extremely site-specific redox process.

The distinction of an SH2 mechanism vs. "redox SE2" sequence is not unlike the distinction between "intrinsic" and "chemical" mechanisms[24] of an inner sphere reaction in which the bridging group is, say, Cl^- or a carboxylate ion. It is a distinction which is difficult to make in the latter case as well, corresponding to the question of whether the electron is transferred via oxidation of Cl^- to $Cl\cdot$, or whether electron transfer from

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one metal center to the other is accompanied by transfer of Cl⁻. Further studies on this point are in progress.

The rates of reduction of the alkylcobalamins are considerably higher than those of the corresponding cobaloximes;[10] k_2 values at 25° are Me 3.6 × 10², compared to 1.4 × 10¹, and Et 4.4, compared to 1.4 × 10⁻². This may reflect a greater strain of the Co–C bond in the cobalamins resulting from the upward-directed substituents on the corrin ring.[25] Similarly the release of alkyl radicals *via* the homolytic scission occurring during photolysis, CoR ⇌ Co^{II} + R·, takes place more rapidly in cobalamins (Me, 5.9 × 10⁻² sec⁻¹) than in cobaloximes (Me, 2.1 × 10⁻³ sec⁻¹).[26]

Formation of the alkylchromium(III) products by a two-step sequence involving first the homolysis of the CoR, followed by the rapid scavenging of R· by Cr²⁺ (R· + Cr²⁺ → CrR²⁺),[27] is clearly ruled out by the form of the rate expression which shows a first-order dependence upon [Cr²⁺].

The reactions of both the Me and Et derivatives occur

with quite negative values of $\Delta S^{\ddagger}$. This indicates a transition state with a highly ordered structure and has been noted previously in processes involving radical transfer.[28]

Experimental Section

Materials. Cyanocobalamin and hydroxocobalamin (Sigma Chemical) were used to synthesize aquo-, methyl-, and ethylcobalamin according to accepted literature procedures.[29] The cobalamins were purified on Bio-Rad Cellex CM cellulose. Cobalamins could be isolated for reuse from reaction solutions or other impure sources using Rohm and Haas XAD-4 macroreticular resin. Chromium(II) perchlorate solutions were prepared from Cr(ClO₄)₃ by reduction with amalgamated zinc.

Procedures. Fresh solutions of the alkyl cobalamins and of Cr²⁺ were made up for each series of experiments. Light was excluded from the former. The solutions were thoroughly freed of oxygen using Cr²⁺-scrubbed nitrogen.

The slower reactions of the ethyl derivative were studied using a Cary 14 spectrophotometer; these reactions were carried out in a 5-cm quartz cell with a rubber serum cap. The more rapid reactions of the methyl derivative were followed using a Durrum stopped-flow instrument.

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Interdimer Exchange in Linear Chain Copper Acetate–Pyrazine[1]

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Abstract: Cu₂Ac₄pyr is shown to contain linear chains of binuclear Cu₂Ac₄ units with a singlet–triplet separation of J = 325 cm⁻¹ and single-crystal epr parameters characteristic of binuclear copper complexes. The pyrazine bridged, interdimer Cu–Cu exchange of J' ∼ 1100 G is deduced from the strong temperature-dependent epr line broadening. The resolved low-temperature hyperfine spectra rule out rapid triplet-excitation motion and, together with interdimer exchange, indicate a difference of at least 0.1 Å in the equilibrium Cu–Cu separation of the singlet and triplet states of Cu₂Ac₄.

The magnetic properties of small transition metal clusters have been intensively studied by both static susceptibility[2] and electron paramagnetic resonance[3] (epr) since Bleaney and Bower's beautiful study of the binuclear copper complex in copper acetate monohydrate,[4] Cu₂Ac₄·2H₂O, which is a member of a large class[3,5] of binuclear copper alkanoates and carboxylates

with antiferromagnetic exchange interactions, J, of about 300 cm⁻¹. It has proved far more difficult[2] to measure exchange interactions, J', *between* clusters, since the usual case of $J' \ll J$ requires very low temperatures, where other approximations are suspect, to detect intercluster exchange. Furthermore, if J' is of the same order as electron dipolar interactions between clusters, then even nmr measurements, as in Cu₂Ac₄·2H₂O, may prove unable to distinguish between intercluster exchange and dipolar contributions.[6]

Intercluster interactions must nevertheless be established in order to identify magnetically one-dimensional polymer systems with more than one metal atom per unit cell. Only the simplest polymer, with one metal atom per unit cell and equally strong exchange with both neighbors, can be identified by measuring a single ex-

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