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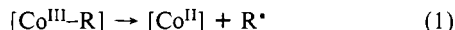
Cobalt-Carbon Bond Disruption Enthalpies: The First Reliable Measurement of a Co-Methyl BDE via Solution Thermochemical Methods†

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Perhaps one of the more basic properties that one can ascribe to a chemical bond is that of bond strength. From the standpoint of predicting new chemical reactions or explaining known chemical reactivities, contributions leading to an understanding of the factors that influence the stability of chemical bonds are highly desirable. This is especially true in the case of metal-carbon (M-C) σ bonds, since such bonds have been implicated as or demonstrated to be integral components of many homogeneous and heterogeneous catalytic cycles,² including those involving the naturally occurring cobalamins.^{3,4}

The groups of Halpern⁵ and Finke,⁶ among others,⁷ have exploited profitably a kinetic method for the determination of absolute Co-C bond disruption energies, $D(\text{Co-C})$, for alkylcobalamins and related model complexes that involves efficient radical scavenging of radical products formed in eq 1 by appropriate radical traps. This approach entails measuring ΔH_1^* for



the forward reaction (1) and assuming that the reverse reaction is essentially diffusion-controlled so that $D(\text{Co-R}) \approx \Delta H_1^* - 2$ kcal/mol; Geno and Halpern⁸ have demonstrated the significant effect of solvent viscosity on the latter assumption. In addition, Koenig and Finke^{6a} have commented on the importance of consideration of the solvent cage effect upon the interpretation of activation parameters derived from solution rate studies, since the efficiency of radical trapping within the solvent cage may vary according to temperature, nature of the solvent, and structure of the metal complex. These authors^{6a} have derived a more explicit relationship for the enthalpy of activation for solution processes typified by reaction 1 that involves the cage efficiency factor, F_c , in order to address this point.

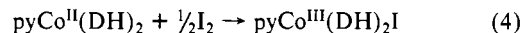
Halpern and co-workers⁹ also have described the utilization of equilibrium thermodynamic methods that do not depend upon the details of the reaction or nature of the solvent for the measurement of $D(\text{Co-R})$ for cobaloxime complexes containing $\text{CH}(\text{CH}_3)\text{R}$ groups. In either of the above cases, the alkyl ligand, R, was generally a relatively large group such as $\text{CH}(\text{CH}_3)\text{R}$, $\text{CH}_2\text{C}(\text{CH}_3)_3$, $\text{CH}_2\text{C}_6\text{H}_5$, or $\text{CH}_2\text{CH}_2\text{CH}_3$.

In this note, we report on the use of iodolytic¹⁰ isoperibol solution calorimetry^{11,12} for the measurement of absolute $D(\text{Co-R})$ values for $\text{pyCo}(\text{DH})_2\text{R}$ (where py = pyridine, DH = the monoanion of dimethylglyoxime, and R = I, CH_3 , $\text{CH}_2\text{C}_6\text{H}_5$, $\text{CH}(\text{CH}_3)_2$). Similar methods have been developed and utilized recently by Marks and co-workers¹⁰ for the determination of absolute U-C bond disruption enthalpies in the $\text{L}_3\text{U}/\text{L}_3\text{U-I}/\text{L}_3\text{U-R}$ system (where L = $\eta^5\text{-(CH}_3)_3\text{SiC}_5\text{H}_4$) and by Hoff and co-workers¹³ in the study of metal-hydrogen bond strengths in the $\text{HM}(\text{CO})_3(\text{C}_5\text{H}_5)$ (M = Cr, Mo, W) system. In this study, we assume that the $\text{pyCo}(\text{DH})_2$ moiety remains basically unchanged so that the enthalpy of iodolysis (ΔH_2 for reaction 2)



$$\Delta H_2 = D(\text{Co-R}) + D(\text{I-I}) - D(\text{Co-I}) - D(\text{R-I}) \quad (3)$$

can be expressed as the difference in bond disruption enthalpies for bonds being made and broken in reaction 2 (see eq 3). $D(\text{I-I})$ is known well,¹⁴ and sufficiently accurate $D(\text{R-I})$ values have been determined.¹⁵ We have utilized redox reaction 4 to obtain the



required value $D(\text{Co-I})$. Equation 4 assumes that no six-coordinate solvato complex forms since toluene should be a poor ligand in this system. The derived $D(\text{Co-R})$ values determined in relatively nonpolar solvents presented here should be a tolerably good approximation (possibly to within 5 kcal/mol) for gas-phase data; conversion to gas-phase numbers can be accomplished if requisite enthalpies of vaporization and sublimation are available or can be estimated.¹²

Experimental Section

Materials and Methods. Bromoform (Aldrich) was washed with water, dried over CaCl_2 , and distilled. It was stored over molecular sieves and copper wire and kept out of direct light. Alkyl halides were used as received from Aldrich, except for benzyl iodide, which was prepared from benzyl bromide and sodium iodide in acetone.¹⁶ Iodine was sublimed under reduced pressure before use.

¹H NMR spectra were obtained on either Varian EM-360A (CW, 60 MHz) or Varian XL-300 (FT, 299.943 MHz) spectrometers. ¹³C NMR spectra were obtained at 75.429 MHz with ¹H decoupling on the latter spectrometer using standard procedures. Magnetic susceptibility measurements were performed on a Johnson-Matthey susceptometer. Magnetic moments were calculated by using literature diamagnetic corrections.¹⁷

The complex $\text{pyCo}^{\text{II}}(\text{DH})_2$ was prepared according to literature procedures.¹⁸ The magnetic moment of the compound was found to be 1.9

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μ_B (average of three trials; lit.^{18b} value 2.0 μ_B); this material was kept under dry, oxygen-free argon or nitrogen (passed through a column of MnO/SiO₂) utilizing standard Schlenk and glovebox practices in order to prevent possible oxidation.

pyCo(DH)₂I was prepared by treating pyCo(DH)₂Cl¹⁹ with excess NaI in refluxing methanol. The product was collected, washed well with water, and air-dried. ¹H NMR (299.943 MHz, CDCl₃): δ 8.20 (d, 2 H, α -H py), 7.71 (t, 1 H, γ -H py), 7.27 (t, 2 H, β -H py), 2.38 (s, 12 H, DH CH₃). ¹³C NMR (75.429 MHz, CDCl₃): δ 153.63 (C=N), 149.87 (α -C py), 138.73 (γ -C py), 125.55 (β -C py), 13.21 (DH CH₃).

The syntheses of Co(DH)(DH₂)Br₂ from CoBr₂·6H₂O and dimethylglyoxime and of pyCo(DH)₂Br from Co(DH)(DH₂)Br₂ and py were accomplished by procedures analogous to those for the Cl complexes.¹⁹ NMR spectral data follow for pyCo(DH)₂Br. ¹H NMR (299.943 MHz, CDCl₃): δ 8.25 (d, 2 H, α -H py), 7.71 (t, 1 H, γ -H py), 7.25 (t, 2 H, β -H py), 2.40 (DH CH₃). ¹³C NMR (75.429 MHz, CDCl₃): δ 152.99 (C=N), 150.65 (α -C py), 138.88 (γ -C py), 125.67 (β -C py), 13.15 (DH CH₃).

The alkyl complexes pyCo(DH)₂R (R = CH₃, CH(CH₃)₂, CH₂C₆H₅) were prepared according to the literature^{19,20} reduction of pyCo(DH)₂Cl with NaBH₄ under an inert atmosphere, followed by addition of the appropriate alkyl bromide or iodide. The known compounds were recrystallized from CH₂Cl₂/petroleum ether and gave satisfactory ¹H NMR spectra.

Reaction of pyCo^{II}(DH)₂ with I₂. In a glovebox, pyCo^{II}(DH)₂ (0.50 g, 1.36 mmol) was loaded into a Schlenk flask equipped with a stirbar. Under Ar flush, dry, degassed toluene (20 mL) was added, followed by I₂ (0.35 g, 1.38 mmol). The mixture was stirred for 1 h, opened to air, and filtered. The product was washed with toluene and petroleum ether; yield 0.624 g (93%). The ¹H and ¹³C NMR (XL-300) spectra of the product were identical with those of an authentic sample of pyCo(DH)₂I prepared as above.

Reactions of pyCo(DH)₂R with I₂. The complexes pyCo(DH)₂R (R = CH₃, CH₂C₆H₅, CH(CH₃)₂) were titrated with I₂ in CHBr₃ in NMR tubes to give rapidly one cobalt macrocyclic product and one organic product by ¹H NMR spectroscopy. The organic product was identified as the corresponding alkyl iodide, RI, by adding a small amount of authentic RI to the NMR tube and observing attendant increases in intensity for the ¹H NMR resonances due to the organic product. Resonances due to RBr are generally quite distinct from those of RI, so positive identification was certain.

We were concerned also about the identity of the product Co complex. Preparative-scale reactions were performed with 0.5 mmol of pyCo(DH)₂R and 0.5 mmol of I₂ in CHBr₃; the product Co compound was precipitated by the addition of petroleum ether and collected in 70–90% yield. Although the 300-MHz ¹H NMR spectra for the products indicated that only one complex was formed in all cases (apparently pyCo(DH)₂I from the chemical shift values), the ¹H NMR spectra for pyCo(DH)₂X (X = I, Br) are somewhat similar (vide supra); however, the identity of the products of the reactions was corroborated unambiguously via their ¹³C NMR spectra. In all cases, the ¹³C NMR resonances of the reaction product complexes were within ± 0.04 ppm of those for authentic pyCo(DH)₂I.

Titration Calorimetry. The anaerobic, isoperibol, solution calorimeter has been described.¹² The procedure used to study the reaction of pyCo(DH)₂ with iodine was similar to that used previously,¹² except iodine was employed as the titrant. The method used to follow the reaction of pyCo(DH)₂R with iodine was slightly different. In brief, sealed ampules containing measured quantities of pyCo(DH)₂R were broken into a calorimeter reaction Dewar filled with iodine-saturated bromoform. In all other aspects, the calorimetric technique used was similar to that previously described.¹²

Results and Discussion

Bromoform was chosen as solvent for the calorimetry experiments involving pyCo(DH)₂R and iodine since the rate of reaction 2 is conveniently fast in this medium. The initial step of this reaction has been demonstrated to occur via oxidation of the starting cobalt complex to charged intermediates.²¹ Thus, the small but significant dipole moment of CHBr₃ presumably helps

Table I. Enthalpies of Solution and of Reaction with Iodine and the Derived Bond Disruption Energies of the pyCo(DH)₂ and pyCo(DH)₂R Complexes (kcal/mol)

compd	ΔH_{soln}^a	$\Delta H_{\text{reacn}}^b$	$D(\text{Co-R})_{\text{soln}}^{b,c}$	R
pyCo(DH) ₂		-32.6 (1.2) ^d	34.6 (1.4)	I
pyCo(DH) ₂ CH ₃	2.9	-19.6 (0.6) ^e	33.1 (1.6)	CH ₃
pyCo(DH) ₂ CH ₂ C ₆ H ₅	2.6	-12.4 (0.9) ^e	31.2 (2.2)	CH ₂ C ₆ H ₅
pyCo(DH) ₂ CH(CH ₃) ₂	2.7	-27.4 (0.8) ^e	21.3 (2.4)	CH(CH ₃) ₂

^a In bromoform solution, 298 K. ^b Quantities in parentheses refer to 95% confidence intervals. ^c Error limits do not include uncertainties that are constant throughout. ^d $\Delta H_{\text{reacn}} = \Delta H_4$ (see text). ^e $\Delta H_{\text{reacn}} = \Delta H_5$ (see text).

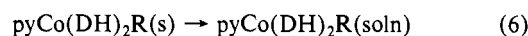
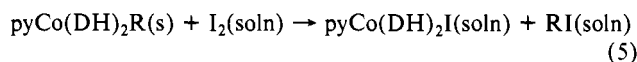
speed up the process. In addition, the reaction rate is dependent upon [I₂];²¹ therefore, the relatively high solubility of I₂ in CHBr₃ also makes it an attractive solvent. We note that the exact mechanism of the iodinolysis reaction is immaterial to the thermochemical measurements,^{10,12} and the nature of the solvent should be of slight impact since it should be noncoordinating in this system and is not very polar.

Moreover, it was apparent from ¹H NMR experiments that the reaction of pyCo(DH)₂R (R = CH₃, CH₂C₆H₅, CH(CH₃)₂) with I₂ in CHBr₃ rapidly and quantitatively produced only one Co-containing product and one organic product. The products were identified unequivocally as pyCo(DH)₂I and RI, respectively, from combined ¹H and ¹³C NMR spectroscopies (see Experimental Section). No trace of brominated compounds was detected, even by 300-MHz ¹H and ¹³C NMR methods.

On the other hand, the reaction of pyCo^{II}(DH)₂ with iodine was studied in toluene under an inert atmosphere since the Co(II) complex can react with alkyl halides such as CHBr₃.^{18b,22} The complex pyCo(DH)₂I is the sole product in accordance with previous observations regarding the reaction of analogous Co(II) compounds with molecular halogens.^{18a,23}

Calorimetry data relevant to eq 3 are presented in Table I. The required $D(\text{I-I})$ ¹⁴ and $D(\text{R-I})$ ¹⁵ values are taken from the literature, and their reported experimental uncertainties are incorporated into our calculations.

The reactions employed in the calorimetric procedure involving the pyCo(DH)₂R species are



In order to obtain the change in enthalpy for the solution-phase process, ΔH_2 , one applies Hess' law and finds that

$$\Delta H_2 = \Delta H_5 - \Delta H_6 \quad (7)$$

The enthalpy change derived via eq 7 is utilized in the calculation of $D(\text{Co-R})$ values (eq 3).

Implicit in our calculations is the assumption that the pyCo(DH)₂ fragment remains structurally unchanged in the various reactants and products. An examination of a large number of molecular structures of pyCo(DH)₂R complexes²⁴ reveals that only the Co-N(py) bond length trans to R should change significantly as a function of R. Although the structure of pyCo(DH)₂I has not been determined, we estimate that the Co-N(py) bond length shortens by ~ 0.05 – 0.10 Å in going from alkyl ligand to iodide (depending upon the nature of the alkyl group) by analogy to the situation in similar aniline complexes.^{24,25} Unfortunately, no crystal structure exists for a five-coordinate Co(II) complex of the bis(dimethylglyoximate) type;²⁶ however, in six-coordinate

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(py)₂Co^{II}(DH)₂,^{27a} [(pyrazine)Co^{II}(DH)₂]_n,^{27b} and [(4,4'-bpy)-Co^{II}(DH)₂]_n,^{27c} the Co-N(py) bond lengths are 2.25, 2.242, and 2.28 Å, respectively. All other structural parameters are essentially the same as for typical Co(III) complexes, so again a shortening of the Co-N(py) bond length (this time by, at most, ~0.20–0.25 Å) is the only major difference. Subtler effects involving movement of the Co ion out of the plane defined by the nitrogen atoms of the DH ligands and adjustments in the dihedral angle between planes defined by the DH ligands are harder to gauge; however, these structural deviations are well cataloged by numerous crystallographic studies in the cobaloxime system and should be small.²⁴ Thus, we believe that relatively little deviation in $D(\text{Co-R})$ data is introduced by our assumption of structural invariance in the pyCo(DH)₂ moiety.

The derived $D(\text{Co-R})$ values in Table I fall within the range of literature values (18–33 kcal/mol) from kinetic^{5–7} and equilibrium⁹ measurements. However, direct one-to-one comparisons between data are not possible since the compounds in this investigation have not been studied previously by the other methods. Our $D(\text{Co-CH}(\text{CH}_3)_2)$ value (21.3 ± 2.4 kcal/mol) is similar to the $D(\text{Co-CH}(\text{C}_6\text{H}_5)\text{CH}_3)$ value of 19.9 kcal/mol in pyCo(DH)₂CH(C₆H₅)CH₃.^{9b} $D(\text{Co-CH}_2\text{C}_6\text{H}_5)$ for pyCo(DH)₂CH₂C₆H₅ is similar to that found for (PhMe₂P)Co(DH)₂CH₂C₆H₅ (30.4 kcal/mol),^{5c} which contains a relatively nonbulky phosphine ligand. For pyCo(saloph)CH₂C₆H₅^{5g} (where saloph = *N,N'*-bis(salicylidene)-*o*-phenylenediamine), $D(\text{Co-CH}_2\text{C}_6\text{H}_5)$ is 22 kcal/mol, which probably reflects a greater cis influence of the relatively electron-rich, nonplanar equatorial saloph ligand.²⁸ In our case, a general weakening of the Co-C bond in the order CH₃ > CH₂C₆H₅ > CH(CH₃)₂ qualitatively follows the trend of increasing size of the alkyl ligand. This is especially true for R = CH(CH₃)₂,²⁹ where the Co-C bond lengthens by about 0.09 Å, as compared to the case for R = CH₃³⁰ (2.085 vs 1.998 Å, respectively).

The $D(\text{Co-CH}_3)$ value (33.1 ± 1.6 kcal/mol) represents, to the best of our knowledge, the first accurate assessment of the metal-to-carbon bond strength for the Co-CH₃ moiety in a vitamin B₁₂ model compound. $D(\text{Co-CH}_3)$ for (H₂O)Co(DH)₂CH₃ has been estimated to be ~47 kcal/mol from photoionization thresholds,³¹ which is clearly a higher number than determined

in the present instance (even allowing for the different trans ligand). Perhaps less applicable, $D(\text{Co}^+\text{CH}_3)$ values of 61 ± 4 and 57 ± 7 kcal/mol have been measured by using ion beam³² and gas-phase photodissociation³³ methods, respectively.

The difference, $D(\text{Co-I}) - D(\text{Co-CH}_3)$, of 1.5 kcal/mol fits the general trend of lower values for this quantity for metals toward the right of the periodic table noted by Marks and co-workers.¹⁰ This effect has been explained as potentially originating in the adaptability of iodide to adjust the polarization of its electrons as the particular bonding situation demands (softness of iodide) or by an increased repulsion (and consequently decreasing attraction) between filled iodine orbitals and metal orbitals as the number of d electrons increases on the metal.¹⁰

Interestingly, for pyCo(DH)₂R, $D(\text{Co-CH}_3)$ is only slightly larger than $D(\text{Co-CH}_2\text{C}_6\text{H}_5)$ although these two values are significantly larger than $D(\text{Co-CH}(\text{CH}_3)_2)$. These observations are perhaps indicative of a relatively small steric trans influence on $D(\text{Co-R})$ by the trans pyridine ligand; it is known from kinetic results that $D(\text{Co-CH}_2\text{C}_6\text{H}_5)$ decreases as the steric bulk of *trans* trialkylphosphine ligands increases in bis(dimethylglyoximate)-cobalt compounds.^{5c} The enhanced stability of metal-benzyl bonds has also been ascribed to possible resonance contributions involving the stable benzyl radical.^{5f} However, we note that $D(\text{M-CH}_2\text{C}_6\text{H}_5)$ is considerably smaller (by 10–20 kcal/mol) than $D(\text{M-CH}_3)$ for organometallic complexes with M = Ti,³⁴ Th,^{12a,b} and U.^{10,12c} Unfortunately no data currently exist for $D(\text{Co-CH}_3)$ in other analogous cobalt complexes for comparison purposes; clearly, more work in this area is required.

In conclusion, the applicability of solution thermochemical methods for the determination of $D(\text{Co-R})$ values in vitamin B₁₂ model compounds has been demonstrated successfully. This approach should prove complementary to the kinetic methods developed by Halpern and co-workers.⁵ In the former, $D(\text{Co-R})$ may be derived for any R group for which $D(\text{R-I})$ (or other suitable group, such as Br or Cl) is known, including smaller R groups such as methyl and ethyl, whereas the kinetic method may be employed in any system producing sufficient quantities of radicals that may be efficiently scavenged, including the biologically important 5'-deoxyadenosyl fragment.^{5d,6b-d}

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- (26) (a) Related five-coordinate complexes include (3,5-lut)Co^{II}(tpp)^{26b} and pyCo^{II}(salen)^{26c} (where 3,5-lut = 3,5-lutidine, tpp = *meso*-tetraphenylporphyrin, and salen = *N,N'*-bis(salicylidene)ethylenediamine) with Co-N axial bond lengths of 2.161 and 2.10 Å, respectively. (b) Scheidt, W. R.; Ramanuja, J. A. *Inorg. Chem.* **1975**, *14*, 2643. (c) Calligaris, M.; Minichelli, D.; Nardin, G.; Randaccio, L. *J. Chem. Soc. A* **1970**, 2411.
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