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Contribution from the Department of Chemistry,
State University of New York at Albany,
Albany, New York 12222, and Department of Chemistry
and Biochemistry, Illinois Benedictine College,
Lisle, Illinois 60532

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

Paul J. Toscano,*[1a] Allen L. Seligson,[1a] Matthew T. Curran,[1a] Andrew T. Skrobutt,[1b] and David C. Sonnenberger*[1b]

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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 Halpern[5] and Finke,[6] among others,[7] have exploited profitably a kinetic method for the determination of absolute Co–C bond disruption energies, D(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 $\Delta H_1^{\ddagger}$ for

$$[\mathrm{Co^{III}{-}R}] \rightarrow [\mathrm{Co^{II}}] + \mathrm{R^{\bullet}} \qquad (1)$$

the forward reaction (1) and assuming that the reverse reaction is essentially diffusion-controlled so that $D(\mathrm{Co{-}R}) \approx \Delta H_1^{\ddagger} - 2$ kcal/mol; Geno and Halpern[8] 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-workers[9] 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(Co–R) for cobaloxime complexes containing $CH(CH_3)R$ groups. In either of the above cases, the alkyl ligand, R, was generally a relatively large group such as $CH(CH_3)R$, $CH_2C(CH_3)_3$, $CH_2C_6H_5$, or $CH_2CH_2CH_3$.

In this note, we report on the use of iodinolytic[10] isoperibol solution calorimetry[11,12] for the measurement of absolute D(Co–R) values for $pyCo(DH)_2R$ (where py = pyridine, DH = the monoanion of dimethylglyoxime, and R = I, CH_3, $CH_2C_6H_5$, $CH(CH_3)_2$). Similar methods have been developed and utilized recently by Marks and co-workers[10] for the determination of absolute U–C bond disruption enthalpies in the $L_3U/L_3U{-}I/L_3U{-}R$ system (where L = η^5-$(CH_3)_3SiC_5H_4$) and by Hoff and co-workers[13] in the study of metal–hydrogen bond strengths in the $HM(CO)_3(C_5H_5)$ (M = Cr, Mo, W) system. In this study, we assume that the $pyCo(DH)_2$ moiety remains basically unchanged so that the enthalpy of iodinolysis (ΔH_2 for reaction 2)

$$\mathrm{pyCo(DH)_2R} + \mathrm{I_2} \rightarrow \mathrm{pyCo(DH)_2I} + \mathrm{RI} \qquad (2)$$

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

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

$$\mathrm{pyCo^{II}(DH)_2} + \tfrac{1}{2}\mathrm{I_2} \rightarrow \mathrm{pyCo^{III}(DH)_2I} \qquad (4)$$

required value D(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(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. ^{13}C 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 $pyCo^{II}(DH)_2$ was prepared according to literature procedures.[18] The magnetic moment of the compound was found to be 1.9

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* To whom correspondence should be addressed.

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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/SiO_2) utilizing standard Schlenk and glovebox practices in order to prevent possible oxidation.

$pyCo(DH)_2I$ was prepared by treating $pyCo(DH)_2Cl$[19] with excess NaI in refluxing methanol. The product was collected, washed well with water, and air-dried. ^1H NMR (299.943 MHz, $CDCl_3$): 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 CH_3). ^{13}C NMR (75.429 MHz, $CDCl_3$): δ 153.63 (C=N), 149.87 (α-C py), 138.73 (γ-C py), 125.55 (β-C py), 13.21 (DH CH_3).

The syntheses of $Co(DH)(DH_2)Br_2$ from $CoBr_2 \cdot 6H_2O$ and dimethylglyoxime and of $pyCo(DH)_2Br$ from $Co(DH)(DH_2)Br_2$ 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, $CDCl_3$): 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 CH_3). ^{13}C NMR (75.429 MHz, $CDCl_3$): δ 152.99 (C=N), 150.65 (α-C py), 138.88 (γ-C py), 125.67 (β-C py), 13.15 (DH CH_3).

The alkyl complexes $pyCo(DH)_2R$ (R = CH_3, $CH(CH_3)_2$, $CH_2C_6H_5$) were prepared according to the literature[19,20] reduction of $pyCo(DH)_2Cl$ with $NaBH_4$ under an inert atmosphere, followed by addition of the appropriate alkyl bromide or iodide. The known compounds were recrystallized from CH_2Cl_2/petroleum ether and gave satisfactory ^1H NMR spectra.

Reaction of $pyCo^{II}(DH)_2$ with I_2. 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 I_2 (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 ^{13}C 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 I_2. The complexes $pyCo(DH)_2R$ (R = CH_3, $CH_2C_6H_5$, $CH(CH_3)_2$) were titrated with I_2 in $CHBr_3$ 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 I_2 in $CHBr_3$; 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 ^{13}C NMR spectra. In all cases, the ^{13}C 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 $CHBr_3$ presumably helps speed up the process. In addition, the reaction rate is dependent upon $[I_2]$;[21] therefore, the relatively high solubility of I_2 in $CHBr_3$ 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.

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]	ΔH_{reacn}[b]	$D(Co–R)_{soln}$[b,c]	R
$pyCo(DH)_2$		−32.6 (1.2)[d]	34.6 (1.4)	I
$pyCo(DH)_2CH_3$	2.9	−19.6 (0.6)[e]	33.1 (1.6)	CH_3
$pyCo(DH)_2CH_2C_6H_5$	2.6	−12.4 (0.9)[e]	31.2 (2.2)	$CH_2C_6H_5$
$pyCo(DH)_2CH(CH_3)_2$	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] $\Delta H_{reacn} = \Delta H_4$ (see text). [e] $\Delta H_{reacn} = \Delta H_5$ (see text).

Moreover, it was apparent from ^1H NMR experiments that the reaction of $pyCo(DH)_2R$ (R = CH_3, $CH_2C_6H_5$, $CH(CH_3)_2$) with I_2 in $CHBr_3$ 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 ^{13}C NMR spectroscopies (see Experimental Section). No trace of brominated compounds was detected, even by 300-MHz ^1H and ^{13}C 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 $CHBr_3$.[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 $D(I–I)$[14] and $D(R–I)$[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

$$pyCo(DH)_2R(s) + I_2(soln) \rightarrow pyCo(DH)_2I(soln) + RI(soln) \tag{5}$$

$$pyCo(DH)_2R(s) \rightarrow pyCo(DH)_2R(soln) \tag{6}$$

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

$$\Delta H_2 = \Delta H_5 - \Delta H_6 \tag{7}$$

The enthalpy change derived via eq 7 is utilized in the calculation of $D(Co–R)$ 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 $pyCo(DH)_2R$ complexes[24] 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(dimethylglyoximato) type;[26] however, in six-coordinate

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$(py)_2Co^{II}(DH)_2$,[27a] $[(pyrazine)Co^{II}(DH)_2]_\infty$,[27b] and $[(4,4'\text{-bpy})Co^{II}(DH)_2]_\infty$[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*(Co–R) data is introduced by our assumption of structural invariance in the $pyCo(DH)_2$ moiety.

The derived *D*(Co–R) values in Table I fall within the range of literature values (18–33 kcal/mol) from kinetic[5–7] and equilibrium[9] 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 $D(Co–CH(CH_3)_2)$ value (21.3 ± 2.4 kcal/mol) is similar to the $D(Co–CH(C_6H_5)CH_3)$ value of 19.9 kcal/mol in $pyCo(DH)_2CH(C_6H_5)CH_3$.[9b] $D(Co–CH_2C_6H_5)$ for $pyCo(DH)_2CH_2C_6H_5$ is similar to that found for $(PhMe_2P)Co(DH)_2CH_2C_6H_5$ (30.4 kcal/mol),[5c] which contains a relatively nonbulky phosphine ligand. For $pyCo(saloph)CH_2C_6H_5$[5g] (where saloph = *N*,*N'*-bis(salicylidene)-*o*-phenylenediamine), $D(Co–CH_2C_6H_5)$ 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 $CH_3 > CH_2C_6H_5 > CH(CH_3)_2$ qualitatively follows the trend of increasing size of the alkyl ligand. This is especially true for R = $CH(CH_3)_2$,[29] where the Co–C bond lengthens by about 0.09 Å, as compared to the case for R = CH_3[30] (2.085 vs 1.998 Å, respectively).

The $D(Co–CH_3)$ 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 $Co–CH_3$ moiety in a vitamin B_{12} model compound. $D(Co–CH_3)$ for $(H_2O)Co(DH)_2CH_3$ 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, $D(Co^+CH_3)$ values of 61 ± 4 and 57 ± 7 kcal/mol have been measured by using ion beam[32] and gas-phase photodissociation[33] methods, respectively.

The difference, D(Co–I) – $D(Co–CH_3)$, 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 coworkers.[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 $pyCo(DH)_2R$, $D(Co–CH_3)$ is only slightly larger than $D(Co–CH_2C_6H_5)$ although these two values are significantly larger than $D(Co–CH(CH_3)_2)$. These observations are perhaps indicative of a relatively small steric trans influence on *D*(Co–R) by the trans pyridine ligand; it is known from kinetic results that $D(Co–CH_2C_6H_5)$ decreases as the steric bulk of *trans* trialkylphosphine ligands increases in bis(dimethylglyoximato)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 $D(M–CH_2C_6H_5)$ is considerably smaller (by 10–20 kcal/mol) than $D(M–CH_3)$ for organometallic complexes with M = Ti,[34] Th,[12a,b] and U.[10,12c] Unfortunately no data currently exist for $D(Co–CH_3)$ 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*(Co–R) values in vitamin B_{12} 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*(Co–R) may be derived for any R group for which *D*(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 $(3,5\text{-lut})Co^{II}(tpp)$[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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