Determination of Co–C bond dissociation energies for organocobalt complexes related to coenzyme B₁₂ using photoacoustic calorimetry

Gang Li,[a] **Fei Fei Zhang,**[b] **Hao Chen,**[a] **Hong Feng Yin,**[a] **Hui Lan Chen** *[a] and **Shu Yi Zhang**[b]

[a] *State Key Laboratory and Institute of Coordination Chemistry, Department of Chemistry, Nanjing University, Nanjing 210093, P. R. China. E-mail: hlchen@nju.edu.cn*
[b] *State Key Laboratory of Modern Acoustics and Institute of Acoustics, Nanjing University, Nanjing 210093, P. R. China*

Photolysis of organocobalt complexes with Schiff base equatorial ligand, bis(salicylidene)ethylenediamine (salen), has been investigated by pulsed, time-resolved photoacoustic calorimetry in methanol at ambient temperature. The observed enthalpy changes and measured cobalt–carbon bond dissociation energies for the above compounds lie within the range 80–170 kJ mol⁻¹. The influence of the steric and electronic factors of both the alkyl group and *trans* base ligand on Co–C bond strength is discussed. It is interesting to note that we obtain the highest Co–CH₃ bond dissociation energy (BDE) value of 168 kJ mol⁻¹ for CH₃Co(salen)H₂O compared with those for coenzyme B₁₂ and its model compounds.

Introduction

Transition-metal alkyl complexes represent an interesting class of organometallic compounds that have potential applications in the areas of both transition-metal catalysis and bioinorganic chemistry. Study of the transition-metal–alkyl bond dissociation energies is crucial for predicting new reactions, explaining reactivities, or understanding chemical reaction mechanisms, which often involve the cleavage and the formation of these bonds. Organocobalt complexes often function as intermediates in the radical polymerization of alkenes and organic substrate transformations *etc.*[1] Furthermore, among them there are a type of widely studied coenzyme B₁₂ model compounds containing a σ-type cobalt–alkyl bond. Coenzyme B₁₂ (5′-deoxyadenosylcobalamin) is one of the few stable organometallic complexes found in nature. It serves as a cofactor for dozens of enzymatic reactions in which 1,2-intramolecular rearrangements of substrates occur. The first step in these reactions is the facile homolytic cleavage of the cobalt–carbon bond of coenzyme B₁₂ to generate a 5′-deoxyadenosyl radical and a Co(II) corrinoid, which is considered to play an essential role in the catalytic cycle.[1–4] Accordingly, a knowledge of the Co–C bond dissociation energy (BDE) of coenzyme B₁₂ and related organocobalt complexes, and of the factors that influence such bond dissociation, is important to an insight into the coenzyme's role. In the past few decades, extensive investigations determining the strength of the cobalt–carbon bond and analyzing the factors which influence it have been carried out on both biologically active cobalamin and organocobalt model compounds.[5–10]

The groups of Halpern,[5] Finke,[6] and others,[7,8] have employed a kinetic method for the determination of the Co–C BDEs of coenzyme itself and related model compounds using appropriate radical traps. This approach entails measuring the activation enthalpy ($\Delta H_1^{\ddagger}$) of the homolytic dissociation reaction of thermolysis for the alkylcobalamin and then deducting the activation enthalpy for viscous flow of solvent ($\Delta H_{\eta}^{\ddagger}$). Halpern and co-workers[9] have also utilized an equilibrium thermo-dynamic method to determine the Co–C BDEs of a series of alkylcobaloxime complexes, which is independent of the details of the reaction or nature of solvent. Toscano *et al.*[10] have reported the calorimetric titration measurement of Co–C BDEs for RCo(DH)₂py (where DH = dimethylglyoxime, py = pyridine) in conjunction with thermochemical cycles.

The above works quantitatively give rise to Co–C BDE values for coenzyme B₁₂ and its model compounds. Their values fall within the range 80–130 kJ mol⁻¹, and depend on the axial and equatorial ligand of those organocobalt complexes.[5–9] Notwithstanding this, it is necessary to extend this work to other organocobalt complexes and to gain a deeper understanding of the relationship between the Co–C bond and structure.

With the development of time-resolved photoacoustic calorimetry (PAC) in the 1980s, it is now feasible to determine the enthalpies that accompany ligand dissociation and/or molecular movements in photoinduced chemical reactions.[11–15] In the PAC experiment, acoustic waves, which are generated from the resulting thermal expansion of the solution after laser excitation, can be detected by the transducer, thus enabling investigation of the energetics of fast photochemical processes. Provided that the mechanism and the quantum yield for the photochemical reaction are well defined, the enthalpy changes accompanying assigned chemical processes can be evaluated. In many cases, this overall enthalpy change may be attributed to the cleavage and/or formation of specific bonds.[14] The utility of the PAC method is that it allows one to determine the metal–carbon bond dissociation energy, even for very high enthalpic values, at room temperature. By using this method we have already determined the Co–C bond dissociation energies in neutral and acidic aqueous solutions for coenzyme B₁₂ and methylcobalamin.[15b] The results are in good agreement with the literature values obtained by kinetic methods.

In the present paper we employed the PAC technique to assess enthalpy changes during the photolysis of alkylcobalt complexes of Schiff bases, RCo(salen)L, in which the equatorial ligand is bis(salicylidene)ethylenediamine (salen). Accordingly, their cobalt–carbon bond dissociation energies were

Table 1 Elemental analyses (%) of RCo(salen)L complexes[a]

Compound	Formula	C	H	N	Co
$CH_3Co(Salen)H_2O$	$C_{17}H_{19}CoN_2O_3$	56.55(56.98)	5.17(5.35)	7.86(7.82)	16.58(16.45)
$CH_3Co(Salen)py$	$C_{22}H_{22}CoN_3O_2$	62.81(63.01)	5.42(5.29)	10.07(10.02)	14.35(14.05)
$CH_3Co(Salen)im^b$	$C_{20}H_{21}CoN_4O_2$	58.62(58.83)	5.16(5.18)	13.90(13.72)	14.52(14.43)
$CH_3Co(Salen)bzim^c$	$C_{24}H_{23}CoN_4O_2$	62.94(62.88)	5.21(5.07)	12.07(12.22)	12.91(12.86)
$C_2H_5Co(Salen)H_2O$	$C_{18}H_{21}CoN_2O_3$	61.12(61.01)	5.47(5.40)	7.73(7.90)	16.72(16.63)
$i\text{-}C_3H_7Co(Salen)H_2O$	$C_{19}H_{23}CoN_2O_3$	58.90(59.07)	5.97(6.00)	7.31(7.25)	15.25(15.25)
$n\text{-}C_4H_9Co(Salen)H_2O$	$C_{20}H_{25}CoN_2O_3$	60.44(59.99)	6.24(6.28)	6.61(6.99)	14.72(14.72)
$i\text{-}C_4H_9Co(Salen)H_2O$	$C_{20}H_{25}CoN_2O_3$	59.71(59.99)	5.80(6.28)	7.04(6.99)	14.70(14.72)

[a] Calculated values in parentheses. [b] im = imidazole. [c] bzim = benzimidazole.

determined. The influence of the axial ligand on the cobalt–carbon bond dissociation energy is discussed both in terms of electronic and steric factors.

Experimental

Materials

Solvent, methanol (AR), was distilled once before use. Ferrocene (AR) was used as calorimetric reference and sublimed once before use. RCo(salen)L were prepared according to the literature[16] and were recrystallized from a methanol–water mixture. Co, C, H, N analyses (%) of the above organo-cobalt derivatives are reported in Table 1. TEMPO (2,2,6,6-tetramethylpiperidinyl-1-oxy) was obtained from Aldrich and sublimed once before use.

Quantum yield measurements

Samples of RCo(salen)L ($\approx 10^{-4}$ M) in methanol with excess TEMPO (≈ 5 mM), were introduced, under anaerobic conditions, into a 10×10 mm quartz cuvette and photochemical studies were carried out at 355 nm. The solution was prepared in this way to ensure that enough TEMPO was present to capture each radical formed and to prevent underestimation of the quantum yield due to diffusion-controlled recombination of Co(II) species and radical. Reactions were monitored at the maximum UV-Vis absorbance change of RCo(salen)L after the laser pulse. The quantum yields, Φ_d, for photolysis of RCo(salen)L were determined with the use of potassium trioxalatoferrate actinometry.[17]

$$\Phi_d = \frac{(\Delta A_s/E_a)\varepsilon_a}{(\Delta A_a/E_a)\Delta\varepsilon_s}\Phi_a \quad (1)$$

Here, $\Delta A_s/E_a$ and $\Delta A_a/E_a$ are the energy-normalized absorbance changes at wavelength λ for the sample solution after the 355 nm laser pulse and for the actinometer at 510 nm, respectively, $\Delta\varepsilon_s$ is the difference in the molar extinction coefficients at the monitoring wavelength λ between RCo(salen)L and Co-(salen)L, ε_a is the molar extinction coefficient of the actinometer at 510 nm, and Φ_a is the quantum yield of the potassium ferrioxalate actinometer. The quantum yields were recorded as the average values from three measurements. In the quantum yield calculations corrections were made for absorption of TEMPO and the Co(II) products.

PAC experiments

The experimental photoacoustic apparatus has been described previously.[11–15] In our experiment a Q-switched Nd:YAG laser (Continuum NP70) operating at 10 Hz, 355 nm, with a pulse width of 8 ns, was used as excitation source. The laser pulse energy was attenuated by means of a set of neutral density filters which allowed the pulse energy to be varied from 5–30 μJ. The laser beam diameter was fixed by a 0.9 mm pinhole, which could determine the time resolution to be equal to the travel

time of the acoustic wave through the laser beam diameter (≈ 600 ns). The acoustic wave induced in solution was detected by a 1.5 MHz PZT piezoelectric transducer. The signal was then amplified by a HP-8847F instrument and recorded on a digitizing oscilloscope (HP-54510B). The data were transferred to a personal computer where each acoustic wave was normalized to the laser pulse energy measured by a transient radiometer (Digi Rad R-752 and P-444). Sample absorbance in methanol ranged from 0.15 to 0.25 at 355 nm (1 cm path length) and was matched to that of a calorimetric reference, ferrocene. Linearity of the signal *versus* excitation energy was observed over the whole range. The waveforms obtained for the sample and reference were unchanged as shown in Fig. 1. The sample solutions were
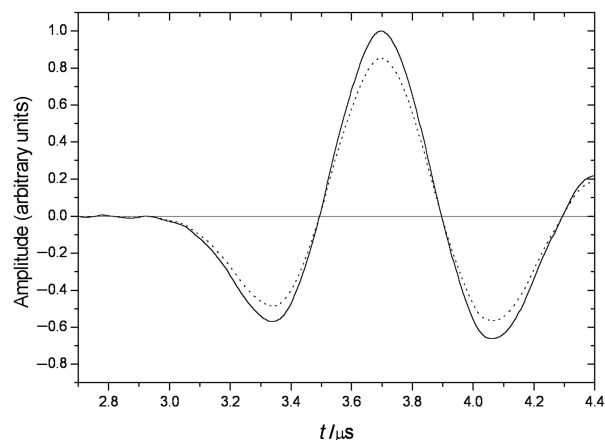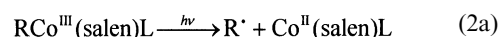

Fig. 1 Energy normalized photoacoustic signals from ferrocene (solid) and $CH_3Co(salen)H_2O$ (dotted) ($\lambda_{exc} = 355$ nm) at 22 °C in methanol.

degassed by bubbling argon for 15 min and maintained under an argon atmosphere during the experiment.

Results

Quantum yields

In order to calculate Co–C bond dissociation energies, quantum yield data for photo-dissociation, Φ_d, of a series of RCo-(salen)L complexes is necessary [see eqns. (4) and (5)]. It is now generally accepted that TEMPO is an efficient scavenger which traps the alkyl radical during the photolysis of alkyl cobalt(III) complexes.[6a,b,18–20] Accordingly, photolysis of $RCo^{III}(salen)L$ forms $Co^{II}(salen)L$ and an alkyl radical. In the presence of radical scavenger (*e.g.*, TEPMO) the latter is effectively trapped with a rate constant[21] of $\approx 10^7–10^9$ M^{-1} s^{-1}.

$$RCo^{III}(salen)L \xrightarrow{h\nu} R^\cdot + Co^{II}(salen)L \quad (2a)$$

$$R^\cdot + TEMPO \xrightarrow{k_T} R\text{-}TEMPO \quad (2b)$$

At present, the quantum yields, Φ_d, for photolysis of RCo(salen)L are determined in methanol under anaerobic conditions at 355 nm, with an added excess of TEMPO trapping

Table 2 Cobalt–carbon bond dissociation energies for alkyl cobalt complexes

R	Chelate	L	Φ_d[c]	Co–C BDE[a]	Ref.
CH_3	salen	H_2O	0.32	168	This work[b]
CH_3	salen	imidazole	0.31	152	This work
CH_3	salen	benzimidazole	0.32	136	This work
CH_3	salen	pyridine	0.29	127	This work
C_2H_5	salen	H_2O	0.31	125	This work
n-C_4H_9	salen	H_2O	0.30	107	This work
n-C_4H_9	salen	—		108	8
i-C_4H_9	salen	H_2O	0.30	90	This work
i-C_3H_7	salen	H_2O	0.29	81	This work
i-C_3H_7	saloph[d]	pyridine		84	5a
i-C_3H_7	$(DH)_2$[e]	pyridine		89	10

[a] In kJ mol^{-1}, error margins ±8 kJ mol^{-1}. [b] This work, measured at 22 °C in methanol under an argon atmosphere. [c] Error margins ± 0.02. [d] saloph = N,N'-bis(salicylidene)-o-phenylenediamine. [e] DH = dimethylglyoxime.

agent, by following the disappearance in absorption of RCo-(salen)L at about 345 nm. The isosbestic points are found at about 310 and 415 nm, respectively, and the final spectrum is consistent with that of an authentic Co^{II}(salen)L species (Fig. 2). It indicates that during photolysis the RCo^{III}(salen)L totally
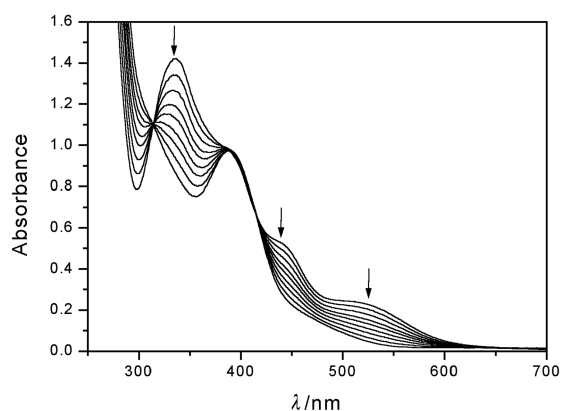
Fig. 2 UV-Vis spectra obtained during the ambient temperature photolysis of $CH_3Co(salen)H_2O$ in methanol in the presence of the radical trap TEMPO.
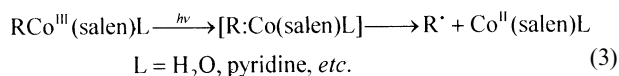
converts into Co^{II}(salen)L, and no side reactions occur. Since the absorbance for R-TEMPO in the visible region is very low, the spectrum in the presence of TEMPO is qualitatively similar to that in its absence. Using the values of $\Phi_a = 1.22$ and $\varepsilon_a(510\ nm) = 1.11 \times 10^4\ M^{-1}\ cm^{-1}$, along with eqn. (1), the quantum yields, Φ_d, for photo-dissociation of RCo(salen)L are obtained (Table 2).

It is interesting to note that the quantum yield values we obtained are in the range of 0.29~0.32. The results indicate that the quantum yields change little while varying the alkyl group in this system. Our value for n-$C_4H_9Co(salen)H_2O$ of 0.30 is in good agreement with the literature value (0.29 in toluene).[22]

Co–C bond dissociation energy

According to previous studies,[18–20,22–24] the mechanism for anaerobic photolysis of organocobalt complexes involves homolytic cleavage of the cobalt–carbon bond to form a geminate pair [Co(II):R] very rapidly. The caged geminate pair can either recombine to form the reactant or diffuse into the solvent to yield free radicals. This means that the Co(II) species and free radical are the final products for our experimental nanosecond to microsecond time window. During the anaerobic photolysis without TEMPO there are some radical side reactions, including hydrogen abstraction by carbon radical from solvent, dimerization, and diffusion recombination, etc. For the sample concentrations of about 10^{-5} M, the concentration of free radicals should be much less than 10^{-5} M. Our photo-dissociation

of the cobalt–carbon bond is not contaminated by artificial side reactions and the apparent enthalpy change is therefore a net enthalpy change from an excited state to form a Co(II) species and a free radical.

$$RCo^{III}(salen)L \xrightarrow{h\nu} [R{:}Co(salen)L] \longrightarrow R^{\bullet} + Co^{II}(salen)L$$
$$L = H_2O,\ pyridine,\ etc. \tag{3}$$

In the case of $CH_3Co(salen)L$, there might be an exchange equilibrium between the axial ligand and solvent (methanol or water). However, the nitrogen donor coordinated form, RCo(salen)L, is predominant,[23,24] since nitrogen donors (e.g., pyridine, imidazole, and benzimidazole) have a much stronger coordination ability for transition-metals than do oxygen donors (e.g., methanol, water). Moreover, it is assumed that only cleavage of the Co–C bond occurs during photolysis, and the axial base ligand still remains on the Co(II) macrocyclic complexes. Therefore, this study only considers the signal contribution from the base ligand coordinated species.

From the photoacoustic waveforms, for example Fig. 1, we have found that RCo(salen)L and ferrocene give identically shaped acoustic waves, furthermore, within the time window of the experiment, ca. 600 ns, the sample acoustic wave does not shift in time relative to the ferrocene wave form. This indicates that all of the observed kinetic processes, which correspond to the homolytic decomposition products of the Co–C bond within our experimental time scale, occur in less than 600 ns and there are no measurable kinetic processes on the time scale of 600 ns to 10 μs. Therefore, the enthalpy changes for photolysis of RCo(salen)L may be attributed to cleavage of the Co–C bond. A plot of the photoacoustic response for CH_3Co-(salen)H_2O in methanol under an argon atmosphere versus pulsed laser intensity is shown in Fig. 3. The corresponding plot for the ferrocene reference is included for comparison. The
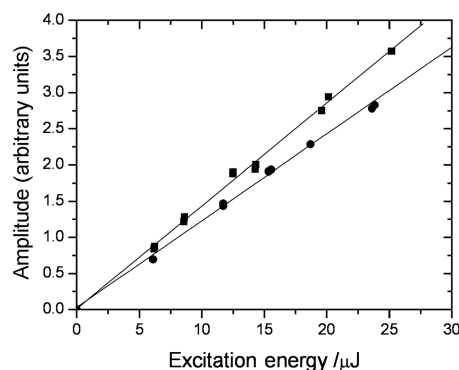
Fig. 3 The relationship between signal amplitude and excitation energy of ferrocene (■) and $CH_3Co(salen)H_2O$ (●) at 22 °C in methanol.

observed reaction enthalpy is related to the term a (defined as the ratio of slopes of the sample and the reference)[14] by eqn. (4), where, E_{hv} is the molar energy of the pulsed laser at 355 nm

$$\Delta H_R = E_{hv}(1 - a)/\Phi_d \qquad (4)$$

(336 kJ mol^{-1}) and Φ_d is the quantum yield for the observed photochemical process. Since RCo(salen)L complexes are relatively rigid, the reaction volume changes during their photolysis are so small that they can be neglected, especially in organic solvents.[12a] In this case, only the Co–C bond cleavage may contribute to the overall enthalpy change, so the Co–C BDE in RCo(salen)L can be estimated by using eqn. (5). The

$$BDE(Co-C) \approx \Delta H_R \qquad (5)$$

Co–C bond dissociation energies for photolysis of a series of RCo(salen)L measured by PAC are given in Table 2. Most of the error in the measurement is derived from the quantum yield. For comparison, the data of related organocobalt complexes from thermolysis kinetic and equilibrium measurements are also listed. The Co–C BDE value for n-C$_4$H$_9$Co(salen)H$_2$O obtained in this work is in excellent agreement with the literature value (108 kJ mol^{-1}) in acetone derived from previous kinetic methods on thermolysis.[8]

Discussion

Previous studies have established that the structural, spectroscopic, thermodynamic and kinetic properties of coenzyme B$_{12}$ model compounds are strongly related to the steric and electronic properties of the axial ligands R and L.[25–28] Electronic effects induced by the *trans* axial ligands, and steric interaction between bulky *trans* axial ligands and equatorial macrocycles are thought to contribute significantly to the Co–C bond strength in organocobalt complexes. For example, with the increase in bulk of R on going from methyl to CH-(CH$_3$)Ph the Co–C BDEs in alkylcobaloxime are decreased by 50 kJ mol^{-1}.[9,10] Furthermore, when R varied from electron-withdrawing ligands, such as CH(CN)Cl, to electron-donating ones, such as i-Pr, the Co–C bond distances lengthen up to about 0.2 Å and log$K$ for L displacement increases by several orders of magnitude.[25] The alkyl cobalt Schiff base complexes appear to have properties closer to cobalamins than do cobaloximes,[29a] however, due to the difficulty in preparing and studying these compounds, they have been less well investigated. The very few available X-ray structural data on RCo(salen)L also show the steric influence of the bulky alkyl ligands on the Co–C and *trans* Co–L bond lengths, as well as the bond angles around the coordinated C atom.[29]

Inspection of the Co–C BDE values of RCo(salen)L complexes measured by photoacoustic calorimetry (see Table 2), reveals the influence of the alkyl group directly bonded to cobalt on Co–C BDE. For a given *trans* ligand, H$_2$O, there is a general trend for weakening of the Co–C BDE in the order CH$_3$ > C$_2$H$_5$ > n-C$_4$H$_9$ > i-C$_4$H$_9$ > i-C$_3$H$_7$ which qualitatively follows the trend of increasing steric bulk of the alkyl ligand and accords with our previous Co–C bond order calculations[30] as well as experimental data[31] for Co–C bond cleavage of RCo-(salen)H$_2$O complexes. In fact, increasing the size of the alkyl group induces the cobalt–carbon bond lengthening or Co–C–C bond angles widening due to conformational distortion of the equatorial ligand away from the alkyl group and towards the *trans* ligand, as a result of Co–C bond weakening.[25,32,33] Thus the large ($\approx$87 kJ mol^{-1}) difference between Co–C BDE of CH$_3$Co(salen)H$_2$O and i-C$_3$H$_7$Co(salen)H$_2$O presumably is mainly due to steric effects. It is noteworthy that the same quantitative decrease in Co–C BDE between methyl and iso-propyl for cobalamin analogues are found.[34] More interestingly, there is an excellent parallel between our order of BDEs for RCo-(salen)H$_2$O and the orders both of rates of Co–C fission and

R	Co–R BDE/kJ mol^{-1}	$10^3 I$	σ^*
CH$_3$	168	−9.00	0.00
C$_2$H$_5$	125	−12.37	−0.100
i-C$_3$H$_7$	81	−15.72	−0.190
n-C$_4$H$_9$	107	−14.07	−0.130
i-C$_4$H$_9$	90	−14.85	−0.125

pKs for displacement of DMBz in alkylcobalamin.[34] Generally, the inductive effect component, I,[35] and the Taft polar substituent constant, σ^*,[36] could qualitatively reflect the electronic effect, as well as both electrostatic and steric effects of the alkyl groups, respectively. In order to provide insight into how steric and electronic factors of alkyl groups affect the Co–C bond dissociation energy of alkylcobalt complexes, it is necessary to assess the influences of the above two constants (Table 3). Plots of Co–C BDE for RCo(salen)H$_2$O *versus* the corresponding I and σ^* values, depicted in Fig. 4, are essentially linear. In the
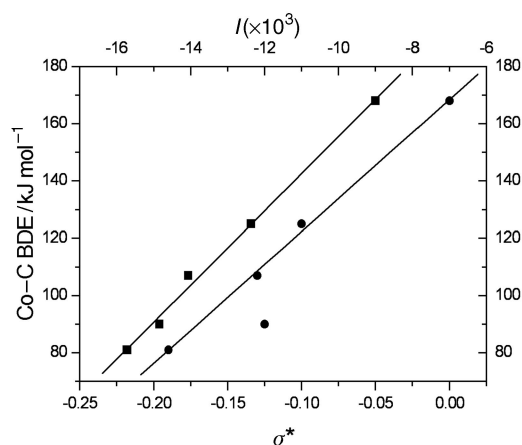
Fig. 4 Relationship between homolytic cobalt–carbon bond dissociation energies and the Taft polar substituent constant, σ^* (●), and the inductive effect component, I (■).

sequence CH$_3$, C$_2$H$_5$, n-C$_4$H$_9$, i-C$_4$H$_9$, i-C$_3$H$_7$, the capability of electronic donation of the alkyl group increases (increasing negative I), so that Co(III) in RCo(salen)L is easily reduced to form Co^{II}(salen)L, and hence, the cobalt–carbon bond dissociation energy decreases. Furthermore, when negative σ^* increases, the steric effect of the alkyl group increases and the stability of the Co–C bond decreases, and hence, the cobalt–carbon bond dissociation energy is decreased.

It has been proposed that both steric and electronic effects of the *trans* base ligand influence the strength of the Co–C bond. In the case of phosphorus donors steric factors would dominate and in the case of nitrogen donors electronic factors would dominate.[27] Measurements of the Co–C BDE for a series of alkylcobaloximes showed that an increase in the basicity of the *trans* nitrogen ligand resulted in an increase in the Co–C BDE.[9] It seems somewhat artificial to specify an exclusive electronic effect for nitrogen donors, however. Although there is no simple linear correlation for different kinds of base ligand of CH$_3$-Co(salen)L, where L (pK_a[37]) is pyridine (5.25), imidazole (6.95), or benzimidazole (5.54), their Co–C BDE values increase following the order of increasing pK_a of the *trans* axial ligand, *i.e.* CH$_3$Co(salen)pyridine < CH$_3$Co(salen)benzimidazole < CH$_3$-Co(salen)imidazole. This trend can probably be explained in terms of the Co–C bond dissociation involving a decrease in oxidation state of cobalt (*i.e.* Co^{III} → Co^{II}). Thus, more basic ligands are expected to stabilize the higher oxidation state, and accordingly, to increase the barrier to homolytic cleavage.[2,9,38] Among these base ligands, imidazole is thought to have the

greater capacity to stabilize higher positive charge by dissipation of its charge over the imidazole ring. Our experimental result is in agreement with the report of Stynes *et al.*,[39] in which they found imidazole stabilized the Co(III)-superoxide porphyrin more than pyridines. It is suggested that the values of pK_a for *trans* base ligands might reflect, at least qualitatively, the corresponding trends of the cobalt–carbon bond dissociation energies. In this case, the present cobalt–carbon BDE for $CH_3Co(salen)H_2O$ is the largest among $CH_3Co(salen)L$ complexes. One possible explanation is that displacement of the *trans* base group by water would make the cobalt atom more electrophilic and, as a result, the alkyl group would be more tightly held.[40] Apparently, any ligand that is able to replace water would decrease the electrophilic character of cobalt and weaken the cobalt–carbon bond. However, to completely elucidate the dependence of dissociation energy on the nature of axial ligand requires further investigation.

Although some Co–CH_3 BDEs have been reported in the literature, for example, that of the base-on methylcobalamin was found to be 155 kJ mol⁻¹ from thermal kinetics by Finke and Martin[6g] and 163 kJ mol⁻¹ from photoacoustic calorimetry by us, the values of Co–C BDE for the base-off methylcobalamin[15b] and $CH_3Co(DH)_2H_2O$[41] are still uncertain but are estimated to be ≥176 kJ mol⁻¹ and ≈196 kJ mol⁻¹, respectively. It is interesting to note that the Co–C BDE value of 168 kJ mol⁻¹ in $CH_3Co(salen)H_2O$ represents, to the best of our knowledge, the accurate determination of the highest cobalt–carbon bond strength in a coenzyme B_{12} model compound.

Conclusion

In this report, we have quantitatively determined Co–C bond dissociation energies for a series of organocobalt(III) Schiff base complexes by using photoacoustic calorimetry, values for which fall in the range of literature values for B_{12} model compounds obtained by kinetic and thermodynamic equilibrium measurements. We have also obtained the highest value of Co–C BDE of $CH_3Co(salen)H_2O$ for coenzyme B_{12} model compounds and discussed the influence of the steric and electronic effects of the axial R and L ligands on the Co–C bond strength. The application of photoacoustic methods to the measurement of cobalt–carbon bond strengths in B_{12} model compounds under mild conditions has been demonstrated successfully. This approach should provide a method complementary to the thermal kinetic or equilibrium methods for determining transition-metal–alkyl bond dissociation energies, and appears to have wide applications.[12b]

On the basis of our results, the organocobalt(III) Schiff base complexes probably represent analogues of the corresponding B_{12} derivatives. Our results also reinforce the view that steric and electronic factors may play an important role in promoting Co–C bond homolysis.

References

1 (*a*) G. W. Parshall and S. D. Ittel, *Homogeneous Catalysis*, Wiley Interscience, New York, 1992, p. 85; (*b*) J. A. Martinho Simões and J. L. Beauchamp, *Chem. Rev.*, 1990, **90**, 629.

2 (*a*) J. M. Pratt, *Inorganic Chemistry of Vitamin B_{12}*, Academic Press, New York, 1972; (*b*) D. Dolphin, ed., B_{12}, Wiley, New York, 1982; (*c*) J. Halpern, *Science*, 1985, **227**, 869 and references therein.

3 (*a*) R. G. Finke, D. A. Schiraldi and B. J. Mayer, *Coord. Chem. Rev.*, 1984, **54**, 1; (*b*) R. G. Finke, in *Molecular Mechanisms in Bioorganic Processes*, eds. C. Bleasdale and B. T. Golding, The Royal Society of Chemistry, Cambridge, 1990, p. 244.

4 L. G. Marzilli, in *Bioinorganic Catalysis*, ed. J. Reedijk, Marcel Dekker, New York, 1993.

5 (*a*) T. T. Tsou, M. Loots and J. Halpern, *J. Am. Chem. Soc.*, 1982, **104**, 623; (*b*) J. Halpern, S. H. Kim and T. W. Leung, *J. Am. Chem. Soc.*, 1984, **106**, 8317; J. Halpern, S. H. Kim and T. W. Leung, *J. Am. Chem. Soc.*, 1985, **107**, 2199; (*c*) M. K. Geno and J. Halpern, *J. Am. Chem. Soc.*, 1987, **109**, 1238; (*d*) S. H. Kim, H. L. Chen, N. Feitchenfeld and J. Halpern, *J. Am. Chem. Soc.*, 1988, **110**, 3120.

6 (*a*) R. G. Finke, B. L. Smith, B. J. Mayer and A. A. Molinero, *Inorg. Chem.*, 1983, **22**, 3677; (*b*) R. G. Finke and B. P. Hay, *Inorg. Chem.*, 1984, **23**, 3041; R. G. Finke and B. P. Hay, *Inorg. Chem.*, 1985, **24**, 1278; (*c*) B. P. Hay and R. G. Finke, *J. Am. Chem. Soc.*, 1986, **108**, 4820; (*d*) B. P. Hay and R. G. Finke, *J. Am. Chem. Soc.*, 1987, **109**, 8012; (*e*) T. W. Koenig, B. P. Hay and R. G. Finke, *Polyhedron*, 1988, **7**, 1499; (*f*) T. W. Koenig and R. G. Finke, *J. Am. Chem. Soc.*, 1988, **110**, 2657; (*g*) B. D. Martin and R. G. Finke, *J. Am. Chem. Soc.*, 1990, **112**, 2419.

7 (*a*) A. Bakac and J. H. Espenson, *J. Am. Chem. Soc.*, 1984, **106**, 5197; (*b*) A. Bakac and J. H. Espenson, *Inorg. Chem.*, 1987, **26**, 4305.

8 S. Wolowiec, S. Balt and W. G. de Bolster, *Inorg. Chim. Acta*, 1991, **181**, 131.

9 (*a*) J. Halpern, F. T. T. Ng and G. L. Rempel, *J. Am. Chem. Soc.*, 1979, **101**, 7124; (*b*) F. T. T. Ng, G. L. Rempel and J. Halpern, *J. Am. Chem. Soc.*, 1982, **104**, 621; (*c*) F. T. T. Ng, G. L. Rempel, C. Mancuso and J. Halpern, *Organometallics*, 1990, **9**, 2762.

10 P. J. Toscano, A. L. Seligson, M. T. Curran, A. T. Skrobutt and D. C. Sonnenberger, *Inorg. Chem.*, 1989, **28**, 166.

11 (*a*) J. A. Westrick, J. L. Goodman and K. S. Peters, *Biochemistry*, 1987, **26**, 8313; (*b*) K. S. Peters and G. J. Snyder, *Science*, 1988, **241**, 1053; (*c*) J. A. Westrick, K. S. Peters, J. D. Ropp and S. G. Sligar, *Biochemistry*, 1990, **29**, 6741; (*d*) K. S. Peters, T. Watson and T. Logan, *J. Am. Chem. Soc.*, 1992, **114**, 4276; (*e*) C. L. Norris and K. S. Peters, *Biophys. J.*, 1993, **65**, 1660; (*f*) A. A. Deniz, K. S. Peters and G. J. Snyder, *Science*, 1999, **286**, 1119.

12 (*a*) S. E. Braslavsky and G. E. Heibel, *Chem. Rev.*, 1992, **92**, 1381; (*b*) M. S. Churio, K. P. Angermund and S. E. Braslavsky, *J. Phys. Chem.*, 1994, **98**, 1776; (*c*) I. Yruela, M. S. Churio, T. Gensch, S. E. Braslavsky and A. R. Holzwarth, *J. Phys. Chem.*, 1994, **98**, 12789; (*d*) P. J. Schulenberg, W. Gärtner and S. E. Braslavsky, *J. Phys. Chem.*, 1995, **99**, 9617; (*e*) J. L. Habib-Jiwan, A. K. Chibisov and S. E. Braslavsky, *J. Phys. Chem.*, 1995, **99**, 10246; (*f*) M. E. Van Brederode, T. Gensch, W. D. Hoff, K. J. Hellingwerf and S. E. Braslavsky, *Biophys. J.*, 1995, **68**, 1101; (*g*) J. L. Habib-Jiwan, B. Wegewijs, M. T. Indelli, F. Scandola and S. E. Braslavsky, *Recl. Trav. Chim. Pays-Bas*, 1995, **114**, 542; (*h*) T. Gensch and S. E. Braslavsky, *J. Phys. Chem. B*, 1997, **101**, 101.

13 (*a*) M. S. Herman and J. L. Goodman, *J. Am. Chem. Soc.*, 1989, **111**, 1849; (*b*) J. L. Goodman and M. S. Herman, *Chem. Phys. Lett.*, 1989, **163**, 417; (*c*) R. R. Hung and J. J. Grabowski, *J. Am. Chem. Soc.*, 1992, **114**, 351.

14 S. T. Belt, J. C. Scaiano and M. K. Whittlesey, *J. Am. Chem. Soc.*, 1993, **115**, 1921.

15 (*a*) S. W. Fu, S. Y. Zhang, G. Li, L. B. Luo and H. L. Chen, *Spectrosc. Lett.*, 1997, **30**, 1395; (*b*) L. B. Luo, G. Li, H. L. Chen, S. W. Fu and S. Y. Zhang, *J. Chem. Soc., Dalton Trans.*, 1998, 2103.

16 (*a*) G. N. Schrauzer, J. W. Sibert and R. J. Windgassen, *J. Am. Chem. Soc.*, 1968, **90**, 6681; (*b*) T. G. Appieton, *J. Chem. Educ.*, 1977, **54**, 443.

17 J. G. Calvert and J. N. Pitts, Jr., *Photochemistry*, John Wiley and Sons, Inc., New York, 1966, p. 783.

18 J. F. Endicott and T. L. Netzel, *J. Am. Chem. Soc.*, 1979, **101**, 4000.

19 (*a*) E. Chen and M. R. Chance, *J. Biol. Chem.*, 1990, **265**, 12987; (*b*) E. Chen and M. R. Chance, *Biochemistry*, 1993, **32**, 1480.

20 K. L. Brown and L. Zhou, *Inorg. Chem.*, 1996, **35**, 5032.

21 (*a*) A. L. J. Beckwith, V. W. Bowry and K. U. Ingold, *J. Am. Chem. Soc.*, 1992, **114**, 4983; (*b*) V. W. Bowry and K. U. Ingold, *J. Am. Chem. Soc.*, 1992, **114**, 4992.

22 R. Blaauw, I. E. Kingma, W. L. J. Werner, S. Wolowiec, J. L. van der Baan, S. Balt, F. Bickelhaupt, M. W. G. de Bolster and G. W. Klumpp, *Inorg. Chim. Acta*, 1998, **269**, 203.

23 J. Gomes and B. de Castro, *Inorg. Chem.*, 2000, **30**, 1994.

24 G. N. Schrauzer, L. P. Lee and J. W. Sibert, *J. Am. Chem. Soc.*, 1970, **92**, 2997.

25 L. Randaccio, *Comments Inorg. Chem.*, 1999, **21**, 327 and references herein.

26 L. Randaccio, N. Bresciani-Pahor, E. Zangrando and L. G. Marzilli, *Chem. Soc. Rev.*, 1989, **18**, 225.

27 N. Bresciani-Pahor, M. Forcolin, L. G. Marzilli, L. Randaccio, M. F. Summer and P. J. Toscano, *Coord. Chem. Rev.*, 1985, **63**, 1.

28 J. M. Pratt, *Chem. Soc. Rev.*, 1985, **14**, 161.

29 (*a*) M. Calligaris, C. Nardin and L. Randaccio, *Coord. Chem. Rev.*, 1972, **7**, 385; (*b*) H. L. Chen, D. Y. Han, T. Li, H. Yan, W. X. Tang, J. Chen, P. J. Zheng and C. Chen, *Inorg. Chem.*, 1996, **35**, 1502.

30 The calculated Co–C bond order of the RCo(salen)H_2O complexes from CNDO/2 calculations are CH_3 > n-C_4H_9 ≈ i-C_4H_9 ≈ n-C_3H_7 > C_2H_5 > i-C_3H_7. See D. Y. Han, H. L. Chen, Q. Miao, M. H. Yu, H. Ni and W. X. Tang, *Chin. Sci. Bull.*, 1994, **39**, 1007.

31 DSC data showed that the cleavage temperature of the Co–C bond for cobalt salen complexes was effected by the steric bulk of the alkyl group in the following order: CH_3 > C_2H_5 > n-C_3H_7 ≈ n-C_4H_9 ≈ i-C_4H_9 ≈ i-C_3H_7. See H. L. Chen, G. Q. Chen, Y. M. Li, W. X. Tang and Q. P. Dai, *Chin. J. Inorg. Chem.–Chinese*, 1991, **4**, 373.

32 L. M. Hansen, P. N. V. P. Kumar and D. S. Marynick, *Inorg. Chem.*, 1994, **33**, 728.

33 (*a*) M. F. Summers, P. J. Toscano, N. Bresciani-Pahor, G. Nardin, L. Randicano and L. G. Marzilli, *J. Am. Chem. Soc.*, 1983, **105**, 6259; (*b*) L. Randicano, N. Bresciani-Pahor, P. J. Toscano and L. G. Marzilli, *J. Am. Chem. Soc.*, 1980, **102**, 7373.

34 S. M. Chemaly and J. M. Pratt, *J. Chem. Soc., Dalton Trans.*, 1980, 2259; S. M. Chemaly and J. M. Pratt, *J. Chem. Soc., Dalton Trans.*, 1980, 2274.

35 G. E. K. Branch and M. Calvin, *The Theory of Organic Chemistry*, Prentice-Hall, New York, 1941, p. 202.

36 R. W. Taft, *J. Am. Chem. Soc.*, 1952, **74**, 3120; R. W. Taft, *J. Am. Chem. Soc.*, 1953, **75**, 4231.

37 R. M. Smith and A. E. Martell, *Stability Constants*, Plenum Press, New York, 1975, vol. 2.

38 S. Nie, P. A. Marzilli, L. G. Marzilli and N. T. Yu, *J. Am. Chem. Soc.*, 1990, **112**, 6084.

39 D. H. Stynes, F. C. Stynes, B. R. James and J. A. Ibers, *J. Am. Chem. Soc.*, 1973, **95**, 1796.

40 W. H. Pailes and H. P. C. Hogenkamp, *Biochemistry*, 1968, **7**, 4160.

41 (*a*) C. Y. Mok and J. F. Endicott, *J. Am. Chem. Soc.*, 1978, **100**, 123; (*b*) J. F. Endicott, K. P. Balakrishnan and C. L. Wong, *J. Am. Chem. Soc.*, 1980, **102**, 5519.