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Mechanistic Information from Pressure Acceleration of Hydride Formation via Proton Binding to a Cobalt(I) Macrocycle

Etsuko Fujita,*,† James F. Wishart,† and Rudi van Eldik*,‡

Chemistry Department, Brookhaven National Laboratory, Upton, New York 11973,
and Institute for Inorganic Chemistry, University of Erlangen-Nürnberg,
Egerlandstrasse 1, 91058 Erlangen, Germany

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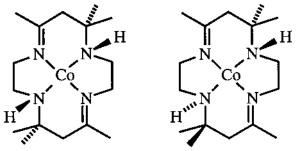
The effect of pressure on proton binding to the racemic isomer of the cobalt(I) macrocycle, CoL^+ (L = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene), has been studied for a series of proton donors using pulse radiolysis techniques. The second-order rate constants for the reaction of CoL^+ with proton donors decrease with increasing pK_a of the donor acid, consistent with a reaction occurring via proton transfer. Whereas the corresponding volumes of activation ($\Delta V^‡$) are rather small and negative for all acids (proton donors) with pK_a values below 8.5, significantly larger negative activation volumes are found for weaker acids (pK_a > 9.5) containing OH groups as proton donors. In the latter case, the observed $\Delta V^‡$ for these protonation reactions show a correlation with the reaction volumes (ΔV°_{ion}) for the ionization of the weak acids with a slope of 0.44, indicating that bond dissociation of the weak acid molecule bound to the metal center proceeds approximately halfway at the transition state along the reaction coordinate in terms of volume changes.

Introduction

Information on the reaction of cobalt(I) complexes with protons is of significant interest for understanding the photo- and electrocatalytic reduction of water to H_2 and of carbon dioxide to HCO_2^-.[1] The cobalt(II) complex CoL^{2+} (L = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene) has received much attention as a catalyst. The complex can exist as stereoisomers *rac*-$[CoL(H_2O)]^{2+}$ and *meso*-$[CoL(H_2O)_2]^{2+}$, both of which have been characterized by X-ray diffraction studies.[2] In organic solvent or in acidic aqueous media significant equilibration between the stereoisomers does not occur, even in one week. However, base-catalyzed equilibration occurs in alkaline aqueous solution with the rate law $-d[meso\text{-}CoL^{2+}]/dt = k[OH][meso\text{-}CoL^{2+}]$, where $k = (5.7 \pm 1.5) \times 10^2\ M^{-1}\ s^{-1}$ at room temperature and pH ≥ 7, favoring the racemic CoL^{2+} isomer at equilibrium.[2] The racemic isomer of the low-spin d^8 Co^IL^+ complex is also thermodynamically favored in both organic and aqueous solutions. The CoL^+ complex is stable in dry CH_3CN solution, but unstable in water due to the involvement of proton transfer to the cobalt(I) center.[3−7] The thermodynamics and kinetics of proton binding (eq 1) to the racemic and meso isomers have been studied in aqueous media using pulse-radiolysis techniques.[3,4,8]



***rac* L** ***meso* L**

$$Co^I(L)^+ + HA + H_2O \rightarrow trans\text{-}Co^{III}(L)(H)(H_2O)^{2+} + A^- \quad (1)$$

Both isomers react rapidly with e^-_{aq} to produce CoL^+. The dependence of the rate constants for reaction 1 on the pK_a

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* To whom correspondence should be addressed. E-mail: (E.F.) fujita@bnl.gov; (R.v.E.) vaneldik@anorganik.chemie.uni-erlangen.de.

† Brookhaven National Laboratory.

‡ University of Erlangen-Nürnberg.

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values of HA has been studied previously.[3,4] Recent work involving the application of high-pressure pulse-radiolysis techniques to various reactions (i.e., oxidation by radicals, oxidative addition, homolysis and heterolysis of metal−carbon bonds, intramolecular electron-transfer processes, etc.)[9] suggested that a systematic study of the effect of pressure on the reaction of CoL^+ with protons and weak acids should provide useful information on the nature of the transition state. We found that the studied reactions are all accelerated by pressure, with the largest effect being observed for the weakest acids. The observed pressure effects are used to draw mechanistic conclusions concerning the formation of the hydride complexes.

Experimental Section

The complex *rac*-$[CoL(H_2O)](ClO_4)_2$ was prepared as previously described[2,10] and characterized by UV−vis and IR spectroscopies and elemental analysis. Although *meso*-$[CoL(H_2O)_2](ClO_4)_2$ has been isolated and characterized,[2] only *rac*-$[CoL(H_2O)](ClO_4)_2$ was used in this study since the equilibration at high pH (>7) is rather rapid. *Warning: The perchlorate salts used in this study may be explosive and potentially hazardous.*

Electron-pulse-radiolysis transient-absorption experiments were carried out with the 2 MeV Van de Graaff accelerator at Brookhaven National Laboratory using a PC-controlled, CAMAC-based data acquisition and control system.[11] The experiments at normal pressure were done using an all-quartz pulse-radiolysis cell consisting of a 50 mL reservoir with an outlet which drains into a 20 mm long, 10 mm high, 5 mm deep rectangular optical cell where the sample is irradiated (through the short dimension) and probed by light passing through the long dimension (2.0 and 6.1 cm path lengths). Irradiated solutions are drained from the cell after use (one or more shots), so the solution in the reservoir remains fresh until it is used. For each pressure-dependence experiment, a sample was placed in a quartz pillbox cell inside a thermostated, four-window high-pressure vessel.[12] One window of the vessel was modified as described elsewhere[13] to enable a sufficient electron pulse to penetrate the sample solution. Since the electron beam penetrates only the first millimeter of the pillbox cell, the solution in the irradiated volume was refreshed between kinetic measurements by stirring with the aid of a magnetic bar inside the pillbox cell, within the high-pressure vessel.

Typical solutions for pulse radiolysis contained a known amount of acid HA, 1 mM *rac*-CoL^{2+}, and 0.5 M *tert*-butyl alcohol, which served as a •OH radical scavenger (eqs 2 and 3). $HClO_4$ or NaOH was added to adjust the pH. Solutions were bubbled with Ar for 20 min and, in the case of the pressure experiments, transferred to a pillbox cell using a syringe. The *rac*-CoL^{2+} complex reacts rapidly with radiolytically produced e^-_{aq} (4.4×10^{10} M^{-1} s^{-1}, eqs 2 and 4) to produce intensely absorbing CoL^+ ($\lambda_{max} = 630$ nm, $\epsilon = 1.1 \times 10^4$ M^{-1} cm^{-1}).[4,8] The *rac*-CoL^{2+} complex also reacts with *tert*-butyl alcohol radicals produced by the scavenging of •OH; however, the reaction is much slower (1.4×10^6 M^{-1} s^{-1})[4] and therefore does not interfere with the reaction of interest. Protonation rate constants were determined by monitoring the first-order decays of CoL^+ at 630 nm. Cobalt(III) hydride can also be formed by reaction of hydrogen atoms with CoL^{2+}. Although this reaction dominates at lower pH (<4) where reaction 5 competes favorably with reaction 4 to increase the H atom yield, the CoL^{2+} concentration and pH conditions were chosen to minimize this effect in the present experiments. The experimental conditions are shown in Table 1

$$H_2O \xrightarrow{\text{2 MeV electrons}} e^-_{aq}, \bullet OH, H\bullet, H_2, H_2O_2 \qquad (2)$$

$$\bullet OH + (CH_3)_3COH \rightarrow H_2O + 0.96(\cdot CH_2)(CH_3)_2COH + 0.04(CH_3)_3CO\bullet \qquad (3)$$

$$e^-_{aq} + CoL^{2+} \rightarrow CoL^+ \qquad (4)$$

$$e^-_{aq} + H^+ \rightarrow H\bullet \qquad (5)$$

Results and Discussion

The second-order rate constants for the reaction of CoL^+ with proton donors in this study and others[3,4] are given in Table 1 and are plotted in the form of log *k* vs pK_a in Figure 1. Figure 1 indicates similar correlations reported previously.[3] Whereas the strong acid H^+ undergoes a diffusion-controlled reaction with CoL^+, the rate constants decrease with increasing pK_a of the donor acid, indicating that the proton-transfer step is rate determining in those reactions. The pK_a of $CoL(H)^{2+}$ was previously determined to be 11.6.[4]

All the studied reactions are accelerated by pressure, and a few typical examples of plots of ln(k_{obs}) versus pressure are shown in Figure 2. The activation volumes ($\Delta V^‡$) for reaction 1 determined from the slope ($= -\Delta V^‡/RT$) of such plots are summarized in Table 1, along with relevant data on the pK_a values of the respective acids, the observed second-order rate constants at ambient conditions, and the reaction volumes associated with the ionization of the acids.[14] The reaction of CoL^+ with H^+ at pH 4−5 (in the presence of *t*-BuOH only) has an observed rate constant of 5×10^4 to 3×10^5 s^{-1} and shows almost no pressure dependence as indicated in Table 1. Above pH 6, the reaction of CoL^+ with H^+ is too slow to interfere with the reactions of interest.

$\Delta V^‡$ remains quite small, negative, and constant for all acids (proton donors) with pK_a values below 8.5 (see Figure 3). Significantly larger negative values are found for weaker acids (pK_a > 9.5), especially those containing OH groups as proton donors. In earlier studies a correlation between the rate of protonation and the acid strength was noted: in general rate constants of above 1×10^7 M^{-1} s^{-1} were found for acids with pK_a values below 7, whereas acids with considerably higher pK_a values showed much lower rate constants, down to ca. 1×10^5 M^{-1} s^{-1} (see Figure 1 and Table 1).

Figure 4, which shows the relationship between the observed activation volume $\Delta V^‡$ for reaction 1 versus the reported $\Delta V°_{ion}$ for ionization of HA,[14] reveals two distinct subsets within the data. For reactions with rate constants in excess of 1×10^7 M^{-1} s^{-1} (largest circles), there is no

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Table 1. Rate Constants and Volumes of Activation for Protonation of CoL^+ by Various Acids (HA)

HA	pK_a	$\Delta V°_{ion}$,[a] $cm^3\ mol^{-1}$	k, $M^{-1}\ s^{-1}$	conditions[b]	pH[b]	$\Delta V^{\ddagger}$,[c] $cm^3\ mol^{-1}$
H_3O^+	1.75		3.1×10^{9} [d]	$HClO_4$[e]	4.07	−1
				$HClO_4$[e]	4.25	−2
				$HClO_4$[e]	4.57	−3
				$HClO_4$[e]	4.95	−1
CH_3COOH	4.5	−12	0.75×10^{8} [d]	0.1 M $NaClO_4$, 1 mM CH_3COOH and 11 mM CH_3COONa	5.92	−4.0
			1.1×10^{8} [f]			
cacodylic acid	6.17	−13.3	2.5×10^{7} (pH 6.3)	4.15 mM cacodylic acid[c]	6.07	−2.8
$H_2PO_4^-$	6.5	−26	0.98×10^{8} [d]	0.1 M $NaClO_4$, 0.5 mM $H_2PO_4^-$ and 0.5 mM HPO_4^{2-}	6.7	−4.0
			0.8×10^{8} [f]			
				0.1 M $NaClO_4$, 2 mM $H_2PO_4^-$ [e]	6.06	−2.8
				0.3 M HPO_4^{2-} [e]	9.34	−5.1
H_2bis-tris-propane	6.75	10.5		40 mM bis-tris-propane[c]	6.89	−2.1
barbital	8.02	−12.5	5.3×10^{7} (pH 7.0)	4 mM barbital[e]	8.20	−3.7
HTRIS	8.07	4.3	1.0×10^{6} (pH 6.7)	20 mM TRIS, 20 mM HTRIS	8.02	−3.7
				30 mM HTRIS[e]	7.36	−3.2
				60 mM HTRIS[e]	7.36	−1.5
HTAPS	8.33	0.5	1.7×10^{5} (pH 7.0)	40 mM TAPS, 40 mM HTAPS	8.33	−5.3
2-ClPhOH	8.55	−11	7.1×10^{7} (pH 7.3)	2.4 mM 2-ClPhOH[e]	8.2	−7.9
				0.89 mM 2-ClPhOH[e]	7.18	−7.9
				1.25 mM 2-ClPhOH[e]	7.8	−6.9
4-ClPhOH			1.1×10^{7} (pH 8.0)			
4-OHPhSO$_3^-$	9.06	−18.4	4.4×10^{7} (pH 8.0)	0.1 M $NaClO_4$, 1 mM 4-OHPhSO$_3^-$	8.30	−8.5
				1 mM 4-OHPhSO$_3^-$	8.37	−9.9
Hbis-tris-propane	9.1	−3.1		80 mM bis-tris-propane[c]	9.08	−6.9
NH_4^+	9.3	7	6×10^{5} (pH 7)	27 mM NH_4^+ [e]	7.56	−4.6
			6.8×10^{5} [d]			
				0.2 M NH_4^+ [e]	8.0	−3.5
H_3BO_3	9.3	−23.7	0.7×10^{5} [d]	0.1M $NaClO_4$, 0.63 M H_3BO_3 and 0.01 M $H_2BO_3^-$	5.6	−15.5
				0.15 M H_3BO_3, 0.15 M $H_2BO_3^-$	9.4	−14.7
PhOH	10.0	−17	3.4×10^{6} (pH 7.9)	17.2 mM PhOH[e]	5.4	−12.3
				9.9 mM PhOH[e]	8.45	−14.8
HCO_3^-	10.3	−27.8	2.5×10^{6} [f]	8 mM HCO_3^- [e]	9.68	−19.0
HPO_4^{2-}	12.25	−24	1×10^{5} [d]	0.1 M $NaClO_4$, 0.095 M PO_4^{3-} and 0.094 M HPO_4^{2-}	11.2	−17.2
				0.095 M PO_4^{3-}, 0.095 M HPO_4^{2-}	11.2	−16.4
				0.3 M HPO_4^{2-} [e]	10.6	−11.0

[a] Reference 15. [b] $[CoL^{2+}] = 1$ mM, 0.5 M *tert*-butyl alcohol, pH for $\Delta V^{\ddagger}$ measurements. [c] The typical experimental error is ±0.5 $cm^3\ mol^{-1}$ except in the case of HA = H_3O^+, for which the error is ±1 $cm^3\ mol^{-1}$. [d] Reference 4. [e] The total amount of HA and A^- is shown. The pH was adjusted by adding NaOH or $HClO_4$. [f] Reference 3.

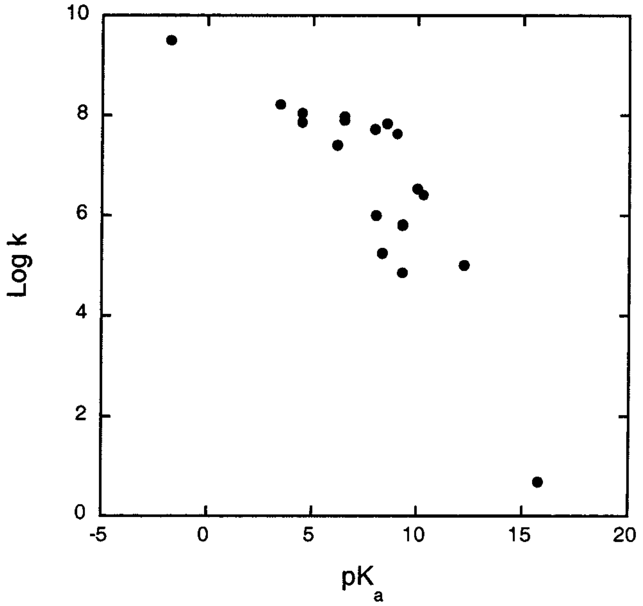

Figure 1. log k for the reaction of CoL^+ with HA versus the corresponding pK_a. The point at the lower right corner corresponds to the reaction of CoL^+ with H_2O. The data were taken from this study and refs 3 and 4.

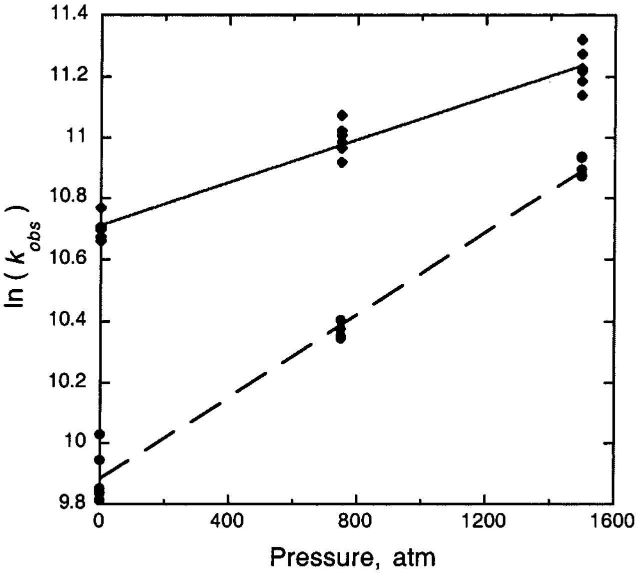

Figure 2. Dependence of ln k_{obs} on pressure: (●) 1 mM CoL^+ and HPO_4^{2-}, $\Delta V^{\ddagger} = -16.4 \pm 0.6\ cm^3\ mol^{-1}$, (◆) CoL^+ and 4-hydroxybenzenesulfonate, $\Delta V^{\ddagger} = -8.5 \pm 0.5\ cm^3\ mol^{-1}$.

correlation of $\Delta V^{\ddagger}$ with $\Delta V°_{ion}$ and the $\Delta V^{\ddagger}$ values tend to cluster between −2 and −5 $cm^3\ mol^{-1}$, with the substituted phenols being a bit more negative. These faster reactions are characterized by smaller absolute $\Delta V^{\ddagger}$ values due to an "early" transition state. In cases where the rate constants for reaction 1 are less than $1 \times 10^{7}\ M^{-1}\ s^{-1}$, the $\Delta V^{\ddagger}$ values become more negative and correlate well with the $\Delta V°_{ion}$

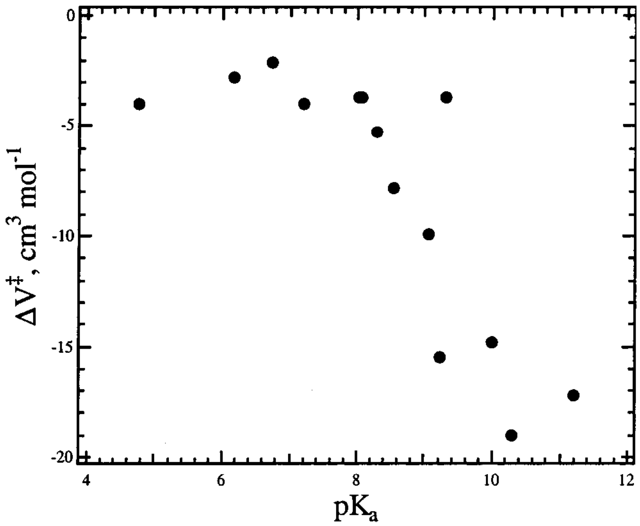

Figure 3. $\Delta V^{\ddagger}$ for the reaction of CoL^+ with HA versus the pK_a of HA.

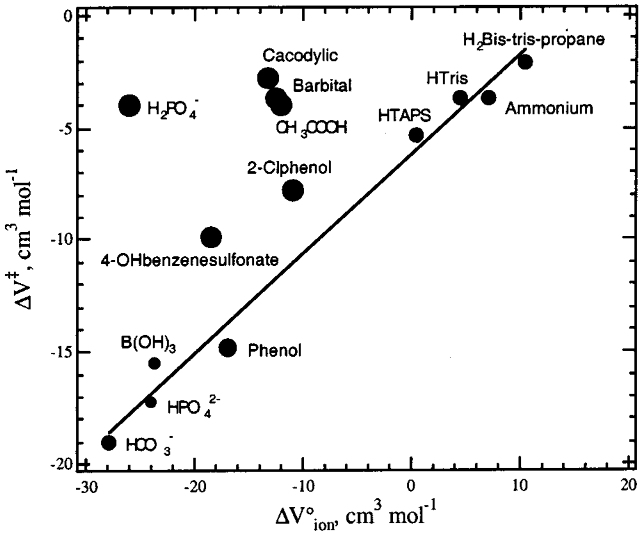

Figure 4. $\Delta V^{\ddagger}$ for the reaction of CoL^+ with HA versus the $\Delta V°_{ion}$ of HA. The size of each marker is correlated to the magnitude of the protonation rate constants given in Table 1. The slope of the plotted line is 0.44.

values. For reactions with slower rate constants, the apparent slope of the plot of $\Delta V^{\ddagger}$ vs $\Delta V°_{ion}$ is 0.44, which indicates that the transition state reflects about half the volume change associated with the ionization of the acid. In this respect it is interesting to note that in an earlier paper[4] a plot of log(k) versus log(K_{eq}) for the reaction with different acids, CO_2 and CO, gave a slope of 0.5, which was interpreted as evidence for an ideal associative (S_N2) reaction. In terms of the volume data reported here, this would mean that HA bond dissociation of the weak acid molecule bound to the metal center proceeds approximately halfway at the transition state along the reaction coordinate in terms of volume changes:

$$Co^{I} + H{-}A \rightarrow [Co^{I}{-}{-}{-}H^{\delta+}{-}{-}{-}A^{\delta-}]^{\ddagger} \rightarrow Co^{III}{-}(H^{-}) + A^{-}$$

Thus, the acid strength/reactivity seems to control the location of the transition state along the reaction coordinate and therefore the value of $\Delta V^{\ddagger}$ in terms of volume changes required to reach the transition state. Furthermore, the intercept of the plot of $\Delta V^{\ddagger}$ vs $\Delta V°_{ion}$, viz., $\Delta V^{\ddagger} = -6 \pm 1$ cm^3 mol^{-1} at $\Delta V°_{ion} = 0$, can be accounted for in terms of an intrinsic volume collapse in the transition state associated with the formation of the Co−HA bond and the formal partial oxidation of the metal center to Co(III). An incipient proton-transfer process from an acid to form a metal hydride has been viewed as a change in hydrogen bonding from A−H---M to A---H−M.[15−20] A number of structural, spectroscopic, and thermodynamic studies of species containing such hydrogen bonds have been published.[15−24] For example, both inter- and intramolecular $R_3N{-}H{-}{-}{-}Co$ hydrogen-bonded species of the anion $[Co(CO)_3L']^-$ ($L' = CO, PR_3$) with amines having different acidities have been studied as geometrical models for the reaction pathway to the formation of the hydride species $HCo(CO)_3L'$.[15] The structural change in $R_3N{-}H{-}{-}{-}Co(CO)_3L'$ associated with changes in the acidity of the amines and the basicity of the metal center is clearly correlated with the proton-transfer pathway. This associative pathway is consistent with our findings.

The overall negative values observed for $\Delta V^{\ddagger}$ can result from a number of contributions:

(a) Bond formation between Co^IL^+ and H^+ (free acid) or HA/XOH will be accompanied by a volume collapse. This may not be very large since the vacant coordination site on Co^IL^+ may already be closely associated with the proton donor in a precursor species.

(b) Bond formation is accompanied by charge transfer to formally oxidize Co(I) to Co(III) and reduce H^+ to H^-. The oxidation of Co(I) to Co(III) could be accompanied by a significant volume collapse if it involves shortening of the Co−L bond length and binding of an additional solvent molecule on forming an octahedral Co(III) complex. Structural data for these complexes suggest that no major change in the Co−N bond length occurs as a function of the oxidation state of the metal center.[25] The overall charge on the complex does not change during this process, so no major changes in electrostriction are expected to contribute toward the $\Delta V^{\ddagger}$ value.

(c) In the case of the reaction of Co^IL^+ with HA/XOH, bond formation between Co^IL^+ and H^+ will be accompanied by (partial) release of A^-/XO^-. Such bond breakage reactions are usually accompanied by a significant decrease in volume due to an increase in electrostriction as a result of charge creation. This volume collapse is clearly reflected by the

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values of $\Delta V°_{ion}$ associated with such reactions. In the case of a protonated amine as proton donor, i.e., R_3NH^+, release of the proton is not accompanied by charge creation and $\Delta V°_{ion}$ is small and positive as a result of an intrinsic volume increase due to N−H bond cleavage. In these cases the $\Delta V^{\ddagger}$ values are very similar to that observed for free H^+.

(d) Protonation of the Co^IL^+ complex can be visualized as an oxidative addition reaction, which is known to be accompanied by significantly negative $\Delta V^{\ddagger}$ values. For instance, oxidative addition of CH_3I to various β-diketonate complexes of Rh(I) exhibits $\Delta V^{\ddagger}$ values between −9 and −25 cm^3 mol^{-1} in various solvents, depending on the solvational contribution resulting from changes in electrostriction associated with the oxidative addition process.[26−28]

The large difference in $\Delta V^{\ddagger}$ for the reactions with $H_2PO_4^-$ and HPO_4^{2-} requires further consideration. The rate constants for these reactions are ca. 10^8 and 10^5 M^{-1} s^{-1}, respectively, i.e., a difference of a factor of 10^3. This must be related to the occurrence of an “early” transition state for the faster reaction with $H_2PO_4^-$ as compared to a “late” transition state for the slower reaction with HPO_4^{2-}. The values of $\Delta V°_{ion}$ are very similar and very negative for both these ions. This means that in the first case the transition state is not controlled by the breakage of the O−H bond (i.e., no significant increase in electrostriction due to charge creation), whereas in the second case the transition state involves significant O−H bond cleavage accompanied by charge creation, i.e., $[Co\text{---}H^+\text{---}OPO_3^{3-}]^{\ddagger}$. The observed $\Delta V^{\ddagger}$ in the latter case is significantly more negative and reflects the ionization occurring during the protonation process.

In the case of the reactions with PhOH and $B(OH)_3$, $\Delta V^{\ddagger}$ was measured at two pH values. For PhOH, the selected pH values (5.4 and 8.45) were lower than the pK_a value (10) and $\Delta V^{\ddagger}$ was found to be independent of pH. In the case of $B(OH)_3$, one pH (9.4) was close to and one (5.6) was below the pK_a value (9.3). Again the $\Delta V^{\ddagger}$ values were found to be independent of the pH, which indicates that the increased dissociation of the weak acid due to the negative $\Delta V°_{ion}$ does not affect the observed pressure dependence. This means that $B(OH)_3$ and $B(OH)_4^-$ must have similar abilities to donate protons to the Co(I) complex.

The observed rate constant does depend on the ammonium ion concentration when a high enough concentration is used to exceed the rate constant for the background reaction under such conditions. The pressure dependence results in a small absolute value for $\Delta V^{\ddagger}$, which is in line with the small positive value calculated for $\Delta V°_{ion}$ associated with the deprotonation of NH_4^+, and the correlation between $\Delta V^{\ddagger}$ and $\Delta V°_{ion}$ for the slower reactions referred to above.

The reported volumes of activation for hydride formation via proton binding to the investigated Co(I) complex clearly demonstrate that fast reactions observed for the stronger acids are accompanied by a small volume collapse in the transition state as a result of the binding of HA to the Co(I) complex. In the case of the slower reactions observed for the weaker acids, the significantly larger volume collapse is ascribed to the partial cleavage of the H−A bond in the transition state $[Co^I\text{---}H^{\delta+}\text{---}A^{\delta-}]^{\ddagger}$, which will be accompanied by an increase in electrostriction due to charge creation. The latter effect does not play a role in proton binding by the stronger acids. Thus, the volumes of activation allow us to comment on the intimate nature of the hydride formation reactions and underline the importance of Co−HA bond formation during this process.

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