

Steric Influences on Cobalt–Alkyl Bond Dissociation Energies

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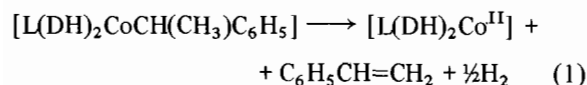
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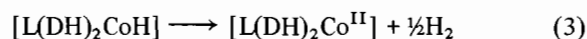
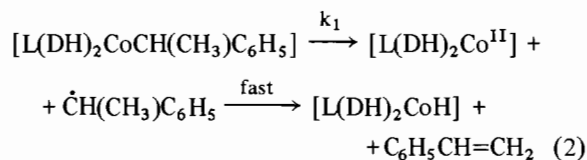
The factors that influence cobalt–alkyl bond dissociation energies are of considerable interest, especially in the context of coenzyme B₁₂-dependent enzymatic processes which are triggered by such bond dissociation [1, 2].

Using the approach that we have previously developed and applied to the elucidation of electronic influences on cobalt–alkyl bond dissociation energies [3, 4], we now report the first direct determination of the influence of steric factors on such bond dissociation energies. Our determinations are based on measurement of the rates and activation enthalpies of reactions depicted by equation (1) (where DH₂ = dimethylglyoxime and L is an axial tertiary phosphine ligand).



We have previously concluded [3, 4] that such reactions proceed through the mechanism of equations (2) and (3) in which homolytic dissociation of the Co–C is the rate-determining step. Since recom-

bination of $[\text{L}(\text{DH})_2\text{Co}^{\text{II}}]$ and $\dot{\text{C}}\text{H}(\text{CH}_3)\text{C}_6\text{H}_5$ is expected to be diffusion-controlled ($\Delta H_{-1}^\ddagger \sim 2$ kcal/mol) the Co–C bond dissociation energy ($D_{\text{Co-R}}$) can be deduced reliably from the measured activation enthalpy of reaction (1), *i.e.*, $D_{\text{Co-R}} = \Delta H_1^\ddagger - 2$ kcal/mol. We have confirmed the validity of this procedure for a variety of $[\text{L}(\text{DH})_2\text{Co-CH}(\text{CH}_3)\text{C}_6\text{H}_5]$ compounds in which L is a nitrogen base (pyridine, imidazole, etc.) [3, 4].



For L = tertiary phosphine, reaction (1) was found to go to completion in acetone or toluene, under N₂, at temperatures from 0 to 45 °C, with no indication of a measurable equilibrium such as had been previously observed when L = pyridine, etc. In some cases, a transient spectral absorbance at 600–610 nm, attributable to the $[\text{L}(\text{DH})_2\text{CoH}]$ intermediate and supportive of the above mechanism, could be detected [5]. Following the procedure previously described [3, 4], the kinetics of reaction (1) were determined and found to conform to the first order rate-law, $-\text{d}[\text{L}(\text{DH})_2\text{CoCH}(\text{CH}_3)\text{C}_6\text{H}_5] = k_1[\text{L}(\text{DH})_2\text{CoCH}(\text{CH}_3)\text{C}_6\text{H}_5]$. Values of k_1 , ΔH_1^\ddagger , ΔS_1^\ddagger and of $D_{\text{Co-R}}$ (deduced from ΔH_1^\ddagger as described earlier) are listed in Table I (arranged in order of increasing k_1 and of decreasing ΔH_1^\ddagger and $D_{\text{Co-R}}$).

The values of k_1 in Table I span a *ca.* 5000-fold range from 1.0×10^{-4} to 4.8×10^{-1} sec⁻¹ at 25 °C. The corresponding ΔH_1^\ddagger values range from 19.3 to 25.9 kcal/mol and of ΔS_1^\ddagger from –1 to +10 cal/mol K while the derived values of $D_{\text{Co-R}}$ range from 17 to 24 kcal/mol. In contrast to the results reported earlier

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TABLE I. Kinetic Data for the Decomposition of $[\text{L}(\text{DH})_2\text{CoCH}(\text{CH}_3)\text{C}_6\text{H}_5]$ in Acetone at 25 °C according to Reaction (1).

No.	L	pK _a	10 ³ k ₁ (25 °C) sec ⁻¹	ΔH ₁ [‡] kcal/mol	ΔS ₁ [‡] cal/mol K	D _{Co-R} kcal/mol
1	P(CH ₃) ₂ C ₆ H ₅	6.5	0.1	25.9	10.5	24
2	P(n-C ₄ H ₉) ₃	8.4	1.2	22.8	5.1	21
3	P(CH ₃)(C ₆ H ₅) ₂	4.6	1.4	–	–	–
4	P(CH ₂ CH ₂ CN) ₃	1.4	3.1	22.1	4.5	20
5	P(C ₂ H ₅)(C ₆ H ₅) ₂	4.6 ^a	3.3	21.3	1.9	19
6	P(C ₆ H ₅) ₃	2.7	19.2	19.3	–1.4	17
7	P(cyclo-C ₆ H ₁₁) ₃	9.7	480 ^b	–	–	–

^aApproximated by pK_a value of P(CH₃)(C₆H₅)₂.

^bEstimated using extrapolated value of ΔH[‡] from Fig. 1 and measured value of k₁ at 5 °C.

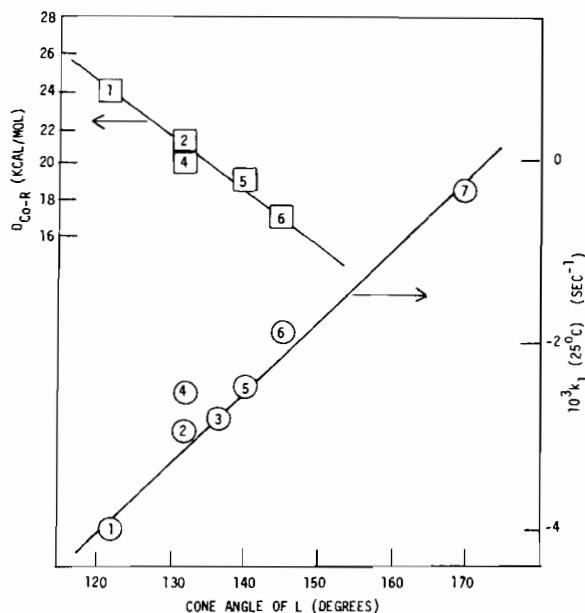


Fig. 1. Dependence of k_1 and of $D_{\text{Co-R}}$ on the cone angle of L (L identified by numbers listed in Table I).

for corresponding complexes in which L = pyridine or a 4-substituted pyridine, neither the rates nor the Co-R bond dissociation energies exhibit any systematic dependence on the basicity of the phosphine ligand as measured by variation in $\text{p}K_{\text{a}}$ from 1.4 to 9.7 [6]. Instead, as revealed by Fig. 1, k_1 increases systematically, while ΔH_1^\ddagger and $D_{\text{Co-R}}$ decrease, with the increasing size of PR_3 as measured by the cone angle [7] of the latter. The magnitude of this dependence is such as to mask the apparently much smaller influence of electronic factors within this series.

The variation of ΔH_1^\ddagger (and of $D_{\text{Co-R}}$), described in Table I and Fig. 1, is somewhat more pronounced than the corresponding variation of k_1 , reflecting a partially compensating variation of ΔS_1^\ddagger (which increases from -1.4 to $+10.5$ cal/mol K while ΔH_1^\ddagger increases from 19.3 to 25.9 kcal/mol). This effect appears to be real since similar compensating trends have been observed for other cobalt alkyl series [3, 4, 8]. While the significance of this is not entirely clear a plausible interpretation is that, in accord with the Hammond postulate [9], the transition state of the bond dissociation process becomes more 'product-like' (i.e., more Co-C bond stretching, hence more positive ΔS_1^\ddagger) as bond dissociation becomes more endothermic.

Our results provide the most impressive and direct evidence to date of the important influence of steric factors on cobalt-alkyl bond dissociation energies in organocobalt compounds that are widely regarded as coenzyme B_{12} models. Such steric influences also are reflected in the results of X-ray structural determinations on $[\text{L}(\text{DH})_2\text{Co-R}]$ compounds which reveal significant Co-C bond lengthening with increasing steric bulk of L (and of R) [10]. These results provide strong support for the view that steric perturbations (for example, enzyme-induced 'upward' distortion of the corrin ring) promote Co-C bond weakening and cleavage in coenzyme B_{12} -dependent enzymic reactions [1, 11, 12, 13].

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