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Invited Paper

Compensation Effects in the Activation Parameters for the Homolytic Dissociation of Transition Metal-Alkyl Bonds

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Determining the activation enthalpies of the homolytic dissociation of transition metal-alkyl bonds constitutes one of the most useful methods of deducing such bond dissociation energies. For several series of organocobalt compounds it has been found that trends of increasing enthalpies of activation for homolytic cobalt-carbon bond dissociation (i.e., of cobalt-carbon bond dissociation energies) are accompanied by partially compensating trends of increasingly positive entropies of activation. Evidence is advanced that these compensation effects are genuine. A suggested explanation is that, with increasing endothermicity of the bond dissociation process, the transition state becomes more "product-like," i.e., further along the path to dissociation.

In 1982[1] we described a method for the determination of transition metal-alkyl bond dissociation energies (D_{M-R}) based on determining the activation enthalpies of the bond-dissociation reaction (Eq. 1) and using the relation of Eq. 2.

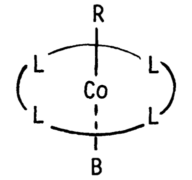
$$L_NM\text{-}R \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} L_NM\cdot + R\cdot \qquad (1)$$

$$D_{M-R} = \Delta H_1^{\ddagger} - \Delta H_{-1}^{\ddagger} \qquad (2)$$

In several cases where this has been tested, the reverse reaction of Eq. 1, i.e., the recombination of $L_NM\cdot$ and $R\cdot$, has been found to be diffusion-controlled.[2,3] Thus, $\Delta H_{-1}^{\ddagger}$ may be approximated by the value of the activation ethalpy for a diffusion-controlled reaction which, in organic solvents of low viscosity such as acetone or toluene, corresponds to about 2 kcal mol^{-1}. Accordingly, in practice, only $\Delta H_1^{\ddagger}$ needs to be determined in such solvents and D_{M-R} may be deduced from the relation,

$$D_{M-R} \approx \Delta H_1^{\ddagger} - 2\ \text{kcal mol}^{-1} \qquad (3)$$

This approach has subsequently been extensively applied by ourselves and others and, indeed, has become one of the most successful and widely used methods for determining transition metal-alkyl bond dissociation energies in solution.[4-8] We have been interested in elucidating the factors that influence such bond energies and that could contribute to the enzyme-induced cobalt-carbon bond weakening and dissociation of coenzyme B_{12} that triggers the latter's biological role. For this purpose we have determined the Co-C bond dissociation energies of an extensive array of octahedral organocobalt(III) compounds [R-Co(Chel)B] (**1**) in which the alkyl group (R), the tetradentate equatorial ligand (Chel) and the *trans*-axial ligand (B) have been systematically varied.[1,3,8,9]



1 (L_4=Chel)

Results and Discussion

Our studies have encompassed various combinations of: R=$C_6H_5CH_2$, $C_6H_5CH(CH_3)$, $CH_3CH_2CH_2$, $(CH_3)_3CCH_2$; Chel=Bis(dimethylglyoximato) $(DH^-)_2$, *N,N′*-bis(salicylidene)-*o*-phenylenediamine (Saloph^{2-}), Octaethylporphyrin (OEP^{2-}); B=pyridine, 4-CN-pyridine, 4-CH_3-pyridine, 4-NH_2-pyridine, PMe_2Ph, PEt_2Ph, PBu_3^n, P(*cyclo*-C_6H_{11})$_3$ and PPh_3. The results of these measurements are summarized in Table 1.

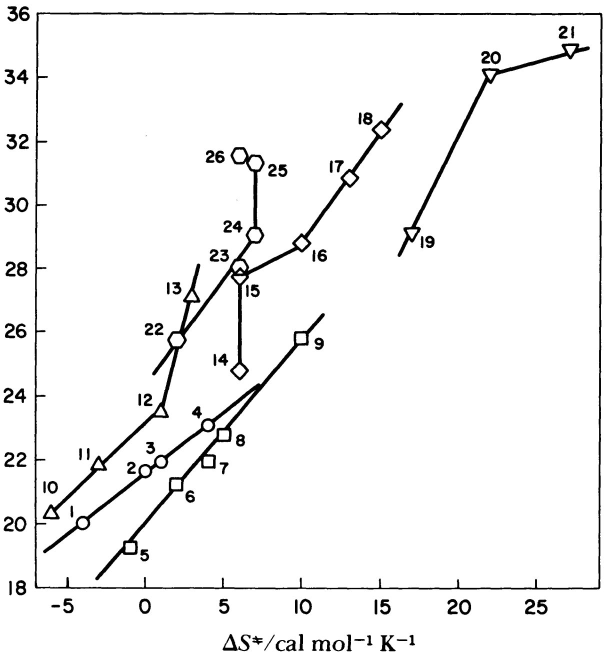


Fig. 1. Relations between enthalpies and entropies of activation for homolytic cobalt-carbon bond dissociation reactions. Numbers refer to entries in Table 1.

Examination of these data reveals that for each series of compounds with a given equatorial ligand, (Chel), variation of either R or B results in a systematic partial "compensation" of the activation parameters such that ΔS^{*} becomes increasingly positive as ΔH^{*} increases. The trends are depicted in Fig. 1.

There are well recognized grounds for treating such "compensation" effects with suspicion since they commonly have an artifactual origin reflecting the interdependence of ΔH^{*} and ΔS^{*}.[11–15] Thus, random errors in the determination of ΔH^{*} for a series of reactions, in which the variation of ΔG^{*} is small, will automatically be reflected in compensating variations in the interdependent variable ΔS^{*} through the relation, $\Delta G^{*}=\Delta H^{*}-T\Delta S^{*}$; hence for $\Delta\Delta G^{*}\approx 0$,

$$\Delta\Delta H^{*} \approx T\Delta\Delta S^{*} \tag{4}$$

or

$$\Delta H^{*} \approx \Delta H_0^{*} + T\Delta S^{*} \tag{5}$$

Several considerations, cited below, lead us to conclude that the trends of dependence of $\Delta S_1^{\ddagger}$ on $\Delta H_1^{\ddagger}$, identified in Table 1 and Fig. 1, are genuine and not of such artifactual origin.

1. The variation of $\Delta H_1^{\ddagger}$ (and, correspondingly, of $\Delta S_1^{\ddagger}$) in each series is not random but increases monotonically with ΔG^{*}. This is contrary to what would be expected if the compensating variations of $\Delta H_1^{\ddagger}$ and $\Delta S_1^{\ddagger}$ had their origins in random errors in the determination of $\Delta H_1^{\ddagger}$.

2. According to Eq. 4 the slopes of plots of ΔH^{*} vs. ΔS^{*} should approximate the mean temperatures ($\bar{T}$) of the measurements. In fact, the slopes of the approximately linear plots of $\Delta H_1^{\ddagger}$ vs. $\Delta S_1^{\ddagger}$ in Fig. 1 are consistently significantly higher than $\bar{T}$. Thus, for the series [PhCH(CH_3)-Co$(DH)_2$(4-X-pyridine)] the slope is ca. 375 K whereas $\bar{T}$=298 K. Similarly, for the series [PhCH(CH_3)-Co$(DH)_2$(PR_3)] the slope is ca. 600 K whereas $\bar{T}$=293 K.

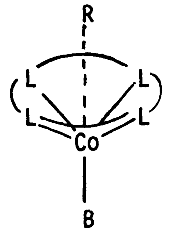
3. Similar trends of dependence of $\Delta H_1^{\ddagger}$ on $\Delta S_1^{\ddagger}$ are observed for several different series of compounds, namely for those in which (Chel)=$(DH^-)_2$, ($Saloph^{2-}$) and (OEP^{2-}) and for different procedures used to determine $\Delta H_1^{\ddagger}$. Furthermore, for one of these series, [PhCH(CH_3)-Co$(DH)_2$(4-X-pyridine)], the validity of

Table 1. Kinetic Data for Cobalt-Alkyl Bond Dissociation Reactions

No.	R	Chel	B	Solvent	Temp range / °C	ΔH_1^{*} / kcal mol^{-1}	ΔS_1^{*} / cal mol^{-1} K^{-1}	Ref.
1	$CH(CH_3)C_6H_5$	$(DH)_2$	4-CN-pyridine	Acetone	14—36	20.1	−4	2
2	$CH(CH_3)C_6H_5$	$(DH)_2$	Pyridine	Acetone	15—35	21.6	0	2
3	$CH(CH_3)C_6H_5$	$(DH)_2$	4-CH_3-pyridine	Acetone	15—35	21.8	1	2
4	$CH(CH_3)C_6H_5$	$(DH)_2$	4-NH_2-pyridine	Acetone	20—35	23.1	4	2
5	$CH(CH_3)C_6H_5$	$(DH)_2$	PPh_3	Acetone	5—25	19.3	−1	9
6	$CH(CH_3)C_6H_5$	$(DH)_2$	$PEtPh_2$	Acetone	25—46	21.3	2	9
7	$CH(CH_3)C_6H_5$	$(DH)_2$	$P(CH_2CH_2CN)_3$	Acetone	10—25	22.1	4	9
8	$CH(CH_3)C_6H_5$	$(DH)_2$	PBu^n_3	Acetone	15—35	22.8	5	9
9	$CH(CH_3)C_6H_5$	$(DH)_2$	PMe_2Ph	Acetone	10—25	25.9	10	9
10	$CH_2C(CH_3)_3$	Saloph	Pyridine	Pyridine	54—69	20.3	−6	1
11	$CH(CH_3)_2$	Saloph	Pyridine	Pyridine	43—63	21.8	−3	1
12	$CH_2C_6H_5$	Saloph	Pyridine	Pyridine	55—65	23.6	1	1
13	$CH_2CH_2CH_3$	Saloph	Pyridine	Pyridine	77—97	27.1	3	1
14	$C_6H_5CH_2$	$(DH)_2$	$P(c\text{-}C_6H_{11})_3$	Toluene	10—46	24.8	6	8
15	$C_6H_5CH_2$	$(DH)_2$	PPh_3	Toluene	47—75	27.8	6	8
16	$C_6H_5CH_2$	$(DH)_2$	$PEtPh_2$	Toluene	50—82	28.8	10	8
17	$C_6H_5CH_2$	$(DH)_2$	PBu^n_3	Toluene	62—100	30.9	13	8
18	$C_6H_5CH_2$	$(DH)_2$	PMe_2Ph	Toluene	66—100	32.4	15	8
19	$C_6H_5CH_2$	$(DH)_2$	$P(c\text{-}C_6H_{11})_3$	Ethylene glycol	35—64	29.1	17	9
20	$C_6H_5CH_2$	$(DH)_2$	PPh_3	Ethylene glycol	47—75	34.1	22	9
21	$C_6H_5CH_2$	$(DH)_2$	$PEtPh_2$	Ethylene glycol	60—88	34.8	27	9
22	$C_6H_5CH_2$	OEP	PPh_3	Toluene	50—70	25.8	2	8
23	$C_6H_5CH_2$	OEP	$PEtPh_2$	Toluene	55—90	28.1	6	8
24	$C_6H_5CH_2$	OEP	PMe_2Ph	Toluene	55—90	29.1	7	8
25	$C_6H_5CH_2$	OEP	PBu^n_3	Toluene	65—100	31.3	7	8
26	$C_6H_5CH_2$	OEP	$P(c\text{-}C_6H_{11})_3$	Toluene	73—91	31.6	6	8

the $\Delta H_1^\ddagger$ values has been supported, using Eq. 2, by independent determinations of $D_{\mathrm{Co-R}}$ based on *thermodynamic* measurements.3)

All of the above argue against the trends of compensating variations of $\Delta H_1^\ddagger$ and $\Delta S_1^\ddagger$, in Table 1 and Fig. 1, having their origin in errors in the determination of $\Delta H_1^\ddagger$. Accordingly, we conclude that these partial compensation effects are genuine and reflect systematic dependencies of structural features of the transition state on $\Delta H_1^\ddagger$. The bond dissociation process associated with $\Delta H_1^\ddagger$ is substantially endothermic and the activation barrier ($\Delta H_{-1}^\ddagger$) associated with the reverse (recombination) is small. Thus, the transition state for the dissociation reaction is anticipated to be "product-like" and to become more so with increasing endothermicity, i.e., with increasing $D_{\mathrm{Co-R}}$ and $\Delta H_1^\ddagger$ (Hammond postulate16)). Since the entropy of the overall dissociation process is substantially positive, it is expected that this should be accompanied by an increase in the entropy of activation, $\Delta S_1^\ddagger$, possibly associated with increasing relaxation of the originally octahedral configuration to the more product-like, less rigid, structure **2**. This provides a plausible explanation for the compensating dependence of $\Delta H_1^\ddagger$ on $\Delta S_1^\ddagger$ that we have identified as a general feature of such transition metal-alkyl bond dissociation reactions.



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In this connection, it is of interest that for the series of complexes, $[C_6H_5CH_2\text{-}Co(OEP)PR_3]$, containing the octaethylporphyrin ligand, which we have previously concluded to be less flexible than the other equatorial ligands,8) $\Delta S_1^\ddagger$ does indeed exhibit the smallest variation.

Thus it is seen that the relation between the bond dissociation rate and bond dissociation energy is not entirely simple. This is of some interest in the context of understanding the nature and origin of the "bond weakening" that is involved in the enzyme-induced Co–C bond dissociation of coenzyme B_{12}.17) Clearly, entropic as well as enthalpic factors may contribute to such bond weakening.

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11) Such grounds for concern are especially cogent with respect to claims of precisely linear dependence of ΔH^* on ΔS^*, i.e., manifestations of the so-called "isokinetic relationship," $\Delta H^* = \Delta H_0^\ddagger + \beta\Delta S^*$, particularly when the value of β is close to the temperature range of measurement. Indeed, there is reason to question the physical plausibility of such an isokinetic relation since it implies reversal of reactivity trends in passing through the "isokinetic temperature." For the purpose of the issues addressed in this paper the precise form of the dependence of ΔH^* on ΔS^* is not of primary importance and we have been careful to avoid claims of "isokinetic" behavior. We do, however, attach relevance to the qualitative monotonic dependence of ΔH^* on ΔS^* that we have observed consistently in the course of these measurements and that we conclude to be genuine.

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