Solvent Dependence of the Activation Enthalpies of Homolytic Dissociation of Metal–Carbon Bonds

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The activation enthalpies for the homolytic cobalt–carbon bond dissociation reactions of several organocobalt compounds in ethylene glycol were found to be 4—6 kcal mol^{-1} higher than in toluene, reflecting the solvent dependence of the activation enthalpy of the reverse recombination process; failure to take account of this solvent dependence can introduce large errors in metal–carbon bond dissociation energies deduced from such kinetic measurements (1 kcal = 4.184 kJ).

In 1982[1] we described a method for determining transition metal–alkyl bond dissociation energies ($D_{\text{M-R}}$), based on measuring the kinetics of reaction (1) and using the relation, $D_{\text{M-R}} = \Delta H^{\ddagger}_{1} - \Delta H^{\ddagger}_{-1}$.

The recombination reaction (k_{-1}), based on cases where this has been ascertained, generally is assumed to be diffusion-controlled.[2] Indeed, we have shown[3] that, at least for acetone and toluene solutions, the data are accommodated by a value of *ca.* 2 kcal mol^{-1}† for ΔH for $\Delta H^{\ddagger}_{-1}$, *i.e.*, a value commonly identified with diffusion-controlled reactions in such solvents and approximated by $\Delta H^{\ddagger}$ for viscous flow.[4]

Subsequently, this approach has been extensively employed by ourselves and others and, indeed, has become the most widely used method for determining metal–alkyl bond dissociation energies in solution.[5—8] Virtually everyone who has used this method has assumed a value of *ca.* 2—3 kcal mol^{-1} for $\Delta H^{\ddagger}_{-1}$. While this does indeed seem to approximate $\Delta H^{\ddagger}_{-1}$ for organic solvents of low viscosity, the well recognized dependence of diffusion rates on viscosity[4] raises serious questions about its appropriateness for more viscous solvents such as ethylene glycol.[6] Accordingly, we now report the results of a comparison of the kinetics of the homolytic bond dissociation reactions of several organocobalt complexes in toluene and in ethylene glycol.

Our study encompasses the determination of the kinetics of homolytic cobalt–carbon bond dissociation reactions of a series of $\text{PhCH}_2\text{–Co(chelate)L}$ complexes [where (chelate)$^{2-}$ = bis(dimethylglyoximato) $(\text{DH}^-)_2$ or octaethylporphyrin (OEP)$^{2-}$ and L is a tertiary phosphine] using 2,2,6,6-tetramethylpiperidineoxy (TEMPO)[5] as the benzyl radical trap, equations (2)—(4).

$$\text{L}_n\text{M–R} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{L}_n\text{M}^{\bullet} + \text{R}^{\bullet} \tag{1}$$

$$[\text{PhCH}_2\text{–Co(chelate)L}] \xrightarrow{k_1} \text{PhCH}_2^{\bullet} + [\text{Co}^{\text{II}}\text{(chelate)L}] \tag{2}$$

$$\text{PhCH}_2^{\bullet} + \text{TEMPO} \longrightarrow \text{PhCH}_2\text{–TEMPO} \tag{3}$$

$$[\text{PhCH}_2\text{–Co(chelate)L}] + \text{TEMPO} \longrightarrow [\text{Co}^{\text{II}}\text{(chelate)L}] + \text{PhCH}_2\text{–TEMPO} \tag{4}$$

Previously we have reported the results of such measurements (determinations of k_1, $\Delta H^{\ddagger}_{1}$, $\Delta S^{\ddagger}_{1}$) on several benzylcobalt compounds in toluene solution.[9] Using the same procedures we now have extended these measurements to ethylene glycol solutions. Our results are reported in Table 1.

For all the systems examined, $\Delta H^{\ddagger}_{1}$ is significantly higher (by 4—6 kcal mol^{-1}) in ethylene glycol than in toluene. Since it seems unlikely that $D_{\text{Co-R}}$ exhibits such a solvent dependence, we conclude that this difference reflects an increase in $\Delta H^{\ddagger}_{-1}$ in going from toluene to ethylene glycol. This is expected for a diffusion-controlled reaction in view of the significantly higher $\Delta H^{\ddagger}$ (viscosity) of ethylene glycol (5.0 kcal mol^{-1} over the temperature range 60—100 °C)[10] compared with that of toluene (1.5 kcal mol^{-1}).[11]

We conclude that the value of $\Delta H^{\ddagger}_{-1}$ exhibits a marked solvent dependence and, in solvents of high viscosity such as ethylene glycol, can be significantly higher than the commonly used value of 2 kcal mol^{-1}. From our measurements it would

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† 1 kcal = 4.184 kJ.

Table 1. Activation parameters for homolytic dissociation of cobalt–carbon bonds.[a]

	Toluene[b]			Ethylene glycol			
[R–Co(chelate)L]	Temp. range/°C	$\Delta H^{\ddagger}_{1}$/ kcal mol^{-1}	$\Delta S^{\ddagger}_{1}$/ cal K^{-1} mol^{-1}	Temp. range/°C	$\Delta H^{\ddagger}_{1}$ kcal mol^{-1}	$\Delta S^{\ddagger}_{1}$/ cal K^{-1} mol^{-1}	$\Delta\Delta H^{\ddagger}_{1}$/ kcal mol^{-1}
[$PhCH_2$–Co(OEP)(Me_2Ph)]	65—100	29.1	7	89—120	33.3	10	4.2
[$PhCH_2$–Co$(DH)_2$(PPh_3)]	47—75	27.8	6	60—88	34.1	22	6.3
[$PhCH_2$–Co$(DH)_2$(P{cyclo-C_6H_{11}}$_3$)]	10—28	24.8	6	35—64	29.1	17	4.3
[$PhCH_2$–Co$(DH)_2$($PEtPh_2$)]	50—82	28.8	10	60—88	34.8	27	6.0

[a] 1 kcal = 4.184 kJ. [b] Data for toluene from ref. 9.

appear that, assuming $\Delta H^{\ddagger}_{-1} = 2$ kcal mol^{-1} for toluene, the appropriate value for ethylene glycol in the range 60—100 °C is *ca.* 4—6 kcal mol^{-1}. Although an alternative explanation has been advanced,[12] we conclude that this accounts for much of the difference of *ca.* 6 kcal mol^{-1} in $\Delta H^{\ddagger}_{1}$ previously reported for homolytic Co–C bond dissociation reactions of 5′-deoxy adenosylcobalamin (coenzyme B_{12}) in water[7] and in ethylene glycol[6] (28.6 *vs.* 34.5 kcal mol^{-1}).

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