Model compounds for co-enzyme B_{12}: the effect of pressure and solvent composition on a cobalt-alkyl bond dissociation reaction

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Abstract

The effect of pressure on the rate of the thermal homolytic fission of the cobalt-carbon bond in the co-enzyme B_{12} model $[C_6H_5CH_2Co(Hdmg)_2P(C_6H_{11})_3]$ has been determined in 1-propanol/water solvent mixtures. The observed volumes of activation are discussed in terms of the cage model and solvent dependence. Homolytic cobalt-carbon bond fission is compared to homolytic carbon-carbon bond fission. It is shown that there is a complete parallel and that the cage efficiency is large.

Introduction

Recently, we reported on the effects of pressure and temperature on the rates of the thermal homolytic fission of the cobalt-carbon bond in some organocobalt model compounds for co-enzyme B_{12} [1].

The investigated model systems comprised six-coordinated benzyl complexes of H_2dmg (dimethylglyoxime or 2,3-butanedione dioxime) with nitrogen and phosphorus coordinated axial ligands and five and six-coordinated butyl complexes of the Schiff base bis(salicylidene)ethylene diamine.

The large positive values found for the volumes of activation could be explained in two, fundamentally different, ways. One of the explanations assumed that the observed volume of activation contained a solvent dependent transport contribution. The 'real' homolytic volume of activation is then much smaller than the observed value, just as found for C-C homolysis [2].

It was concluded that more data were needed, particularly with water as solvent. Obviously, solubility problems are then expected and we therefore decided to use a solvent mixture.

The present paper describes the effect of pressure on the rate of the thermal homolytic fission of the cobalt-carbon bond in the model compound $[C_6H_5CH_2Co(Hdmg)_2P(C_6H_{11})_3]$ in 1-propanol/water solvent mixtures.

Experimental

Details about the experimental set-up have been described before [1].

The measurements were carried out photometrically at 375 nm and at a temperature of 55 °C. Reactions were followed for at least three half-lives and two independent runs were made. The complex concentration was varied between 3×10^{-5} and 6×10^{-5} M and the tricyclohexylphosphine (PCy_3) concentration between 3×10^{-2} and 6×10^{-2} M. The solutions were kept at pH = 6.4 using a 10^{-1} M sodium acetate/acetic acid buffer. Because 1-propanol functions as a radical trap itself [3], no trap was added. From the pressure dependence of the rate constant (5-7 measurements in the range of 0.1 to 150 MPa) the volume of activation was calculated on the basis of the formula: $\ln k_{obs} = A + BP + CP^2$ whereby $\Delta V^{\neq}_{obs} = -BRT$ and $\Delta\beta^{\neq}_{obs} = 2CRT$ [4-6]. In all cases the second order term gave a significant increase in the accuracy of the fit.

The fate of the cobalt(II) product formed upon homolysis has to be carefully and independently checked in all solvent mixtures, to exclude possible interference with the homolysis reaction. In this way it was found that pyridine and

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tributylphosphine cannot be used in this solvent system as axial ligand. Tricyclohexylphosphine presented no problems of this type.

Results and discussion

The general scheme of homolytic fission uses the cage model [2, 7–12]. The application of this model to organometallic chemistry has recently been advocated [13–15].

$$\underset{}{[\mathrm{Co{-}C}]} \underset{k_c}{\overset{k_1}{\rightleftharpoons}} \underset{\text{cage pair}}{[\mathrm{Co^{\bullet}\ {}^{\bullet}C}]} \underset{k_{-1}}{\overset{k_d}{\rightleftharpoons}} \underset{\text{free radicals}}{[\mathrm{Co^{\bullet}}] + [\mathrm{C^{\bullet}}]}$$

$$\xrightarrow{\text{trap}} \text{trapped products}$$

This scheme describes the homolytic fission of the cobalt–benzyl bond in $[C_6H_5CH_2Co(Hdmg)_2PCy_3]$ resulting in a cobalt(II) product and a (trapped) benzyl radical. The overall process (homolysis followed by cage escape) is indicated by k_{obs}. The homolysis step is described by k_1, the recombination of the initial geminate radicals (cage return) by k_c, the diffusive cage escape (separative diffusion) by k_d and cage re-entry by k_{-1}. In the presence of a radical trap the k_{-1} route will be swamped and the observed rate constant will be given by [2, 14]

$$k_{obs} = k_1\left(\frac{k_d}{k_c + k_d}\right)$$

Now, three situations should be recognized, depending on the cage efficiency [14]

$$F_c = \left(\frac{k_c}{k_c + k_d}\right)$$

If the cage efficiency is large due to $k_c \gg k_d$, k_{obs} will be given by

$$k_{obs} = \left(\frac{k_1 k_d}{k_c}\right)$$

and $\Delta V^{\neq}_{obs} = \Delta V^{\neq}_1 - \Delta V^{\neq}_c + \Delta V^{\neq}_d$

If the cage efficiency is negligible due to $k_d \gg k_c$, k_{obs} will be given by: $k_{obs} = k_1$ and $\Delta V^{\neq}_{obs} = \Delta V^{\neq}_1$.

Finally, for an intermediate cage efficiency the original formula should be used

$$k_{obs} = k_1\left(\frac{k_d}{k_c + k_d}\right)$$

and

$$\Delta V^{\neq}_{obs} = \Delta V^{\neq}_1 + RT\delta \ln\left[1 + \frac{k_c}{k_d}\right]\Big/\delta P$$

Arguments have been presented that organometallic systems show large cage efficiencies [13–15], larger than those for previously studied organic radical pairs. The present case is no exception in this aspect. This can be argued as follows. If the situation of negligible cage efficiency would apply, $\Delta V^{\neq}_{obs}$ would be solvent independent. Earlier results [1] and results presented here (see later) show that this is not so. The case of intermediate cage efficiency has already been discussed by Swaddle and co-workers [16, 17] for some organometallic chromium(III) complexes. It was shown that in this case the apparent volume of activation could never decrease with increasing pressure. However, just as found by Swaddle and co-workers [16], $\Delta V^{\neq}_{obs}$ does decrease markedly with increasing pressure in our situation, which must originate in the intrinsic pressure dependence of the activation volume(s).

It follows thus that the situation is best described by a large cage efficiency: $\Delta V^{\neq}_{obs} = \Delta V^{\neq}_1 - \Delta V^{\neq}_c + \Delta V^{\neq}_d$. Assuming that besides the diffusion barrier no extra barrier to escape from the cage exists, $\Delta V^{\neq}_d$ will be equal to the pseudo volume of activation for diffusion, $\Delta V^{\neq}_\eta$ (also called the transport contribution), given by [12, 18]: $\Delta V^{\neq}_d = \Delta V^{\neq}_\eta = RT\delta \ln \eta/\delta P$.

For 1-propanol/water mixtures, the viscosity has been measured in dependence of composition, temperature and pressure [19]. Therefore, $\Delta V^{\neq}_\eta$ can be calculated.

The observed activation parameters and the calculated $\Delta V^{\neq}_\eta$ are listed in Table 1. It is obvious from this Table that $\Delta V^{\neq}_{obs}$ is solvent dependent. In Fig. 1 we have plotted $\Delta V^{\neq}_{obs}$ *versus* the calculated value of $\Delta V^{\neq}_\eta$. From this it follows that $\Delta V^{\neq}_1 - \Delta V^{\neq}_c (= \Delta V^{\neq}_{obs} - \Delta V^{\neq}_d)$ is small but positive. Now it is known that $\Delta V^{\neq}_c$ is small but negative, typical values reported for organic homolysis range from -1 to $-4\,\mathrm{cm^3\,mol^{-1}}$ [8, 10]. It can therefore be concluded that $\Delta V^{\neq}_1$, the 'real' homolytic volume of activation, is also small. This behaviour mimicks C–C homolysis,

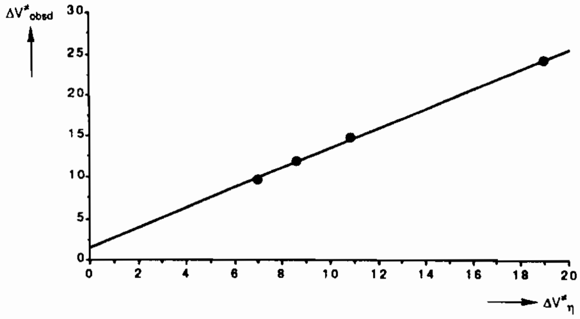

Fig. 1. The observed volume of activation ($\Delta V^{\neq}_{obs}$) for cobalt–carbon bond dissociation of $[C_6H_5CH_2Co(Hdmg)_2PCy_3]$ as a function of the calculated volume of activation for diffusion ($\Delta V^{\neq}_\eta$) in 1-propanol/water mixtures at 55 °C. Values are in $\mathrm{cm^3\,mol^{-1}}$.

TABLE 1. Activation parameters for cobalt–carbon bond dissociation of $[C_6H_5CH_2Co(Hdmg)_2PCy_3]$[a] in 1-propanol/water mixtures at 55 °C

Mixture (wt.%) water:1-propanol	$\Delta V^{\neq}_{obs}$ ($cm^3\ mol^{-1}$)	$\Delta\beta^{\neq}_{obs}$ ($cm^3\ mol^{-1}\ MPa^{-1}$)	$\Delta V^{\neq}_{\eta}$[b] ($cm^3\ mol^{-1}$)
10:90	24.42 ± 1.71	0.125 ± 0.022	18.96
40:60	14.80 ± 1.21	0.076 ± 0.015	10.84
50:50	11.97 ± 1.30	0.059 ± 0.017	8.60
60:40	9.67 ± 0.61	0.091 ± 0.011	6.96

[a] H_2dmg = 2,3-butanedione dioxime; PCy_3 = tricyclohexylphosphine. [b] Calculated (see text).

for which the work of Neuman [2] indicates that the transition states for homolytic scissions are in the order of 2 to 3% larger in volume than the ground state initiators. In fact, the behaviour of this organometallic co-enzyme B_{12} model expressed in Co–C homolysis parallels completely the cage effect and activation volumes for organic homolytic scission reactions [2, 7–11] with a very efficient cage. This reinforces the conclusions reached by Koenig and Finke [13, 14] on cage effects in organotransition metal chemistry.

Combining the present results with those presented earlier [1] it can be said that for both non-aqueous and aqueous systems cobalt–carbon bond homolysis in uncharged co-enzyme B_{12} models is characterized by a very efficient cage, a small intrinsic volume of activation and a solvent dependent observed volume of activation that can be quite large.

In this aspect it is rather surprising that Swaddle and co-workers [16, 17] reported strongly positive volumes of activation for some simple organometallic cobalt(III) and chromium(III) complexes in aqueous solution for which $\Delta V^{\neq}_{\eta} = 0.16\ cm^3\ mol^{-1}$ [18]. It could be that for these charged species desolvation effects are much more important.

Even more interesting is the question of how the present results relate to cobalt–carbon bond homolysis in the co-enzyme B_{12} system. We are currently investigating this matter.

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References

1 S. Wolowiec, S. Balt and M. W. G. de Bolster, *Inorg. Chim. Acta, 181* (1991) 131.
2 R. C. Neumann, Jr., *Acc. Chem. Res., 5* (1972) 381.
3 R. Yamada, S. Shimizu and S. Fukui, *Biochim. Biophys. Acta, 124* (1966) 195.
4 T. Asano and W. J. Le Noble, *Chem. Rev., 78* (1978) 381.
5 D. A. Palmer and H. Kelm, *Coord. Chem. Rev., 36* (1981) 89.
6 R. van Eldik, T. Asano and W. J. Le Noble, *Chem. Rev., 89* (1989) 549.
7 R. C. Neuman Jr. and J. V. Behar, *J. Am. Chem. Soc., 91* (1969) 6024.
8 R. C. Neuman Jr. and R. J. Bussey, *J. Am. Chem. Soc., 92* (1970) 2440.
9 W. A. Pryor and K. Smith, *J. Am. Chem. Soc., 92* (1970) 5403.
10 R. C. Neuman Jr. and J. V. Behar, *J. Org. Chem., 36* (1971) 654 and 657.
11 D. D. Tanner and P. M. Rahimi, *J. Am. Chem. Soc., 104* (1982) 225.
12 J. Schroeder and J. Troe, *Chem. Phys. Lett., 116* (1985) 453.
13 Th. W. Koenig and R. G. Finke, *J. Am. Chem. Soc., 110* (1988) 2657.
14 Th. W. Koenig, B. P. Hay and R. G. Finke, *Polyhedron, 7* (1988) 1499.
15 B. D. Martin and R. G. Finke, *J. Am. Chem. Soc., 112* (1990) 2419.
16 M. J. Sisley, W. Rindermann, R. van Eldik and Th. W. Swaddle, *J. Am. Chem. Soc., 106* (1984) 7432.
17 K. Ishihara and Th. W. Swaddle, *Can. J. Chem., 64* (1986) 2168.
18 N. S. Isaacs, *Liquid Phase High Pressure Chemistry*, Wiley, New York, 1981.
19 W. Weber, *Rheol. Acta, 14* (1975) 1012.