A study of the cage mechanism for the homolytic cleavage of the cobalt–carbon bond in coenzyme B_{12} by varying the solvent viscosity

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Abstract

The effect of viscosity on the rates of anaerobic thermal and photolytical scission of the cobalt–carbon bond in coenzyme B_{12}($AdoB_{12}$) has been determined in different water/glycerol mixtures. The photolysis of the coenzyme is compared with [adenosylcobinamide]$^+OH^-$. Using a simple diffusion model, the fractional cage efficiency and the rate of recombination of the radicals trapped in the solvent cage could be determined from the viscosity dependence of the reaction rates. The activation parameters for the cage recombination were derived from the temperature dependence of the recombination reaction giving $\Delta H^{\ddagger} = 17.9 \pm 0.8$ kJ mol^{-1} and $\Delta S^{\ddagger} = -21 \pm 2$ J K^{-1} mol^{-1}. The results obtained are shown to be relevant to the discussion about the Co–C bond dissociation energy of $AdoB_{12}$, for which a combination of our results with published data gives 119 ± 8 kJ mol^{-1}.

Introduction

The photolytic cleavage of the Co–C bond in coenzyme B_{12} is accepted to proceed by a simple homolytic mechanism [1], as long as the pH is kept high enough to prevent an acid-catalyzed reaction. Photolysis is retarded by protonation of the benzimidazole group of the ligand [2]; a recent study [3] shows a decrease in quantum yield by a factor of 5 on protonation. Thermal reactions show similar behavior [4–7]. For the thermal reactions it has been shown that adenosylcobalamin, at 100 °C, in aqueous solution at pH = 7 and in neat ethyleneglycol gives 5′-deoxyadenosine and the cyclization product 8,5′-anhydroadenosine [7, 8]. Adenosylcobalamin in neutral polyglycol–water mixtures may be assumed to give similar products as reported for the neat solvents. Endicott and Netzel [9] were the first to establish experimentally a cage pair intermediate for this reaction. Their study has recently been extended by Chen and Chance [3]. The cage mechanism is attracting fresh attention for the interpretation of homolytic fission in organometallic chemistry in general [10, 11] and in coenzyme B_{12} in particular [11, 12].

The relevant kinetics and thermodynamics for the thermal and photochemical cage model have now been worked out in detail [13]. For the dissociation of the coenzyme, further denoted as $AdoB_{12}$ (Ado = 5′-deoxyadenosyl), the complete scheme is

$$AdoB_{12}(\text{base-off}) \overset{K}{\rightleftharpoons} AdoB_{12}(\text{base-on}) \quad (1)$$

$$AdoB_{12}(\text{base-on}) \underset{k_c}{\overset{k_1}{\rightleftharpoons}} \overline{[Ado^{\cdot}\,B_{12}]} \underset{k_{-1}}{\overset{k_d}{\rightleftharpoons}} Ado^{\cdot} + B_{12r} \quad (2)$$

cage pair free radical

K is defined as $K = [AdoB_{12}(\text{base-on})]/[AdoB_{12}(\text{base-off})]$ and, as the base-off form may be protonated, is pH dependent. The scheme given is simplified by the general [12, 14–16] and recently established assumption that for thermal reactions the base-on form ($AdoB_{12}$(base-on), where the pendent 5,6-dimethylbenzimidazole ligand of the coenzyme is axially coordinated to Co) is much more reactive (≈ 100 times) than the base-off form. The picture does not show essential differences between thermal and photochemical reactions, with the exception that the difference in quantum yield between the base-on and the base-off form is only a factor of 5, compared to a factor of 100 for the thermal reactions [17]. In the presence of a radical scavenger (such as tempo = 2,2,6,6-tetramethylpiperidine 1-oxide)**, both the reverse (k_{-1}) route and the radical cycli-

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**The nitroxide trap method has been developed by Finke and coworkers. For a recent survey of key features of this trap see ref. 8, especially the refs. 8 and 13 therein.

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zation [7] will be swamped. The observed rate constant for the disappearance of $AdoB_{12}$ will then be given by [11]:

$$k_{obs} = \frac{K}{1+K} \times k_1 \times \frac{k_d}{k_c + k_d} \quad (3)$$

As both K and k_1 are nearly solvent independent[5], studying the decomposition reaction in mixtures of chemically related solvents with diverging viscosities will primarily influence the rate of diffusion from the cage (k_d), thus giving the opportunity to unravel the mechanism. We report here a photochemical and thermal study of $AdoB_{12}$ and [adenosylcobinamide]$^+OH^-$([AdoCbi]$^+OH^-$), the base-free derivative of $AdoB_{12}$, in mixtures of the protic solvents water and glycerol, enabling the described analysis.

Experimental

Materials

Adenosylcobalamin (Fluka) and tempo (Aldrich) were used without further purification. The purity was tested by UV–Vis spectroscopy. [Adenosylcobinamide]$^+OH^-$ was prepared according to Hay and Finke [17]. The purity was tested by UV–Vis, ^1H NMR and FAB-MS spectroscopy. The solvents were purchased as analytical grade, if necessary dried by routine methods, and deoxygenated by three freeze/pump/thaw cycles.

Methods and measurements

All experiments were performed in an inert (nitrogen gas) atmosphere; the oxygen level did not exceed 5 ppm. The setup for the thermal reactions has already been described [5]. The thermal decomposition of the coenzyme was studied at 380.6 K in a concentration of $5–10 \times 10^{-5}$ M in a tris(hydroxymethyl)aminomethane buffer at pH = 8.0 under 10 MPa pressure to prevent boiling of the solvent. For the photochemical experiments the agitated solution was irradiated in a thermostatted (within 0.2 °C) compartment with a 150 W Oriel xenon arc lamp at 40 cm; at regular time intervals the spectrum of an aliquot was measured. In all cases the absorbance at 376 and 524 nm obeyed a first-order rate law for at least 3 half-lives within 3%. Reproducibility was within 5% for at least 2 independent runs. Independence of the measured rates on buffer and tempo concentrations and pH was checked. Viscosities were taken from ref. 18.

Results and discussion

Reaction conditions and products

As the reaction rate of adenosylcobalamin did not change over a pH range of 7.0–8.5, all reactions were carried out at pH = 8.0, with the exception of one control experiment at 10^{-2} M $HClO_4$, where the base-off form is the main species. In all cases tempo was used as radical scavenger in a 10^{-2} M concentration (at least a 100 fold excess). Under these conditions all adenosyl radicals are trapped by tempo. We did not find any evidence in the UV–Vis spectra of a reaction of B_{12r} with tempo as stated by Hay and Finke [7]; the sole corrinoid reaction product in water and water/glycerol mixtures was B_{12r} (UV–Vis), indicated by isosbestic points at 385, 490 and 580 nm. The reaction products for photolysis and thermolysis are identical. At the pH used there is no significant change in the base-on/base-off pre-equilibrium in the different solvent mixtures (calculated between 95% and 91% base-on according to ref. 7), indicated by a constant absorption at 524 nm in the different solvent mixtures [15].

Dependence of rate on viscosity

Our analysis starts from eqn. (3). As indicated, k_1 and K are solvent independent to a very good approximation. For k_1 this is not surprising in view of the nature of the cage formation process (no change in solvation) and the manifest closed microenvironment [19, 20] of the coenzyme.

The rate of diffusion from the cage will only depend on the viscosity of the solvent. This property has been introduced some time ago as the viscosity test [21, 22] for the homolysis cage mechanism. We based our analysis of the process of diffusion from the cage on the Smoluchowski–Stokes–Einstein treatment of recombination [23]. The assumptions in our model are that the coenzyme is static in the solvent cage compared to the adenosyl radical (the volume of the coenzyme is approximately 6 times the volume of the adenosyl radical) and that there is no extra (non-diffusional) barrier to escape from the cage. Scaling the model to the diffusional radius of the adenosyl radical ($a = 440$ pm), which has been determined experimentally [24], a reasonable assumption in view of generally used models [23] seems that recombination (k_c^0) can occur for distances smaller than $2a$ and that radicals will be effectively trapped by tempo at $4a$. This leaves an intermediate region for diffusion towards the trap. On reaching the steady state, k_d is given by eqn. (4).

$$k_d = 3D/8a^2 \quad (4)$$

The dependence of k_d on the viscosity of the solvent is obtained from the Stokes–Einstein equation [23] (eqn. (5)).

$$D = kT/6\pi\eta \tag{5}$$

We then have:

$$\frac{k_d}{k_c} = \left(\frac{k_d^0}{k_c^0}\right)\frac{T}{\eta} \tag{6}$$

with $k_d^0 = k/8\pi a^3 = 6450$ Pa s K^{-1}.

The results of the model are, of course, dependent on the choice of parameters. For instance, the extremes for the diffusion region $4a$–$6a$ and a–$6a$ change the value for k_d^0 to 1930 and 19 340, respectively. It is worth noting that Stokes' law has been shown to be only valid for molecules large compared to the solvent molecules [25]; this makes this approximation a good one for the large molecules we are studying. For thermal reactions eqn. (3) then in an obvious notation [13] becomes:

$$k_{obs} = \frac{k_{1t}k_{dt}}{k_{ct}+k_{dt}} = \frac{k_{1t}}{1+\left(\frac{k_c^0}{k_d^0}\right)\frac{\eta}{T}} \tag{7}$$

Obviously k_{1t} is a composite parameter, incorporating the pre-equilibrium. For photochemical reactions the case is slightly more complicated. To start with, it must be emphasized that our choice of the photochemical method had the only object of rapidly generating a cage pair in larger concentrations than possible in a classical flash photolysis experiment, thus increasing the accuracy of the rate constants obtained. This is only possible if the recombination is not photoreactive. The reverse assumption that k_c is photoactive and consequently temperature independent, as used by Loginov *et al.* [26] in an analogous analysis of the photodecomposition of alkylcobaloximes, does not seem realistic. In order to test the photoactivity of the recombination reaction we did the following experiment. In the assumption that the formation of the cage radical pair (k_1) and the recombination reaction of this radical pair (k_c) are viscosity independent, we tentatively put:

$$k_{obs}(I, \eta) = \frac{k_{1p}(I)k_{dp}(\eta)}{k_{cp}(I)+k_{dp}(\eta)} \tag{8}$$

where I and η indicate dependence on light intensity and viscosity, respectively. For the present the contribution from the base-off form is neglected, but we will come back to this point later. The photoactivity of $k_{cp}(I)$ may be tested by comparing the ratio of observed rate constants for the most diverging values of η at two significantly different light intensities. We did this for the coenzyme in water ($\eta_1 = 8.90\times10^{-4}$ Pa s) and 90 wt.% glycerol ($\eta_2 = 0.164$ Pa s) at two different light intensities ($I_2 \approx 6I_1$).

The results are:

$$k_{obs}(I_1, \eta_1)/k_{obs}(I_1, \eta_2) = 7.60\times10^{-3}/2.53\times10^{-4} = 30$$
$$\text{error } \pm 0.2$$

$$k_{obs}(I_2, \eta_1)/k_{obs}(I_2, \eta_2) = 4.51\times10^{-2}/1.56\times10^{-3} = 29$$
$$\text{error } \pm 0.5$$

This proves k_{cp} to be photoinactive within the experimental error.

The results of the thermal and photochemical experiments are collected in Table 1. The values for the thermal reaction are in good agreement with the values found by Hay and Finke [7]*. Due to the slow reaction rate it was necessary to perform the experiments at high temperature. To prevent boiling the experiments were carried out under 10 MPa pressure. The effect of this pressure on the diffusion model is negligeable, as the pressure dependence of the viscosity in water and water/glycerol mixtures is small (0.04% for water on going from 0.1 to 100 MPa) [27].

The general equation $k_{obs} = \alpha_1/(1+\alpha_2\eta)$ (based on eqn. (7)) gives a very good fit to each series at a fixed temperature, as shown for a representative case in Fig. 1. The parameter α_2 can be interpreted as k_c^0/Tk_d^0. The results of the fit are collected in Table 2. From these values k_c can be calculated using eqn. (6): $k_c = 4\times10^8$ s^{-1} (with a variation between 10^8 s^{-1} and 10^9 s^{-1} for the extremes defined above) at 298 K.

In view of the assumptions made in either of the models, this value is in good agreement with the value found by Endicott and Netzel: $1.3\pm1\times10^9$ s^{-1} [9].

Comparison between $AdoB_{12}$ and $[AdoCbi]^+OH^-$

A comparison between cobalamin and cobinamide is especially interesting, as our analysis can bring out whether the lower reactivity towards Co–C scission of the latter compound is caused by a reduction of k_1, and increase of k_c, or a combination of both (see eqn. (3)). In agreement with the published [3] quantum yields, the quantum yield for the base-off form is 5.1 ± 1.9 times lower than the quantum yield for the base-on form, the base-off form of $AdoB_{12}$ reacts about five (5.2 ± 0.1) times slower photo-

*Hay and Finke's values of $\Delta H^\ddagger = 129.3\pm1.7$ kJ/mol and $\Delta S^\ddagger = 20.1\pm3.3$ J/mol K in water at pH = 7.0 extrapolate to 1.59×10^{-4} s^{-1} at $T = 380.6$ K.

TABLE 1. Kinetic data for cobalt–carbon bond dissociation reactions of $AdoB_{12}$ and $[AdoCbi]^+OH^-$ in glycerol/water mixtures

Glycerol (wt.%)	Photolysis $10^3 \times k_{obs}$ (s^{-1})				Thermolysis $10^4 \times k_{obs}$ (s^{-1})
	$AdoB_{12}$			$[AdoCbi]^+OH^-$	$AdoB_{12}$
	298.2 K	308.2 K	323.2 K	298.2 K	308.6 K
0.0	33.4	41.5	48.5	6.39	2.24
10.0	33.0			6.08	1.92
30.0		35.6	41.7	5.24	1.76
50.0	21.0	24.7	29.9	3.52	1.41
67.5	10.7	15.2	20.0	1.80	
70.0					0.96
75.0	5.81	10.1	16.1	1.07	
80.0	3.15	6.97	10.2	0.64	0.876
85.0	1.95	4.07	6.80		
90.0	1.69	2.98	4.14		0.566

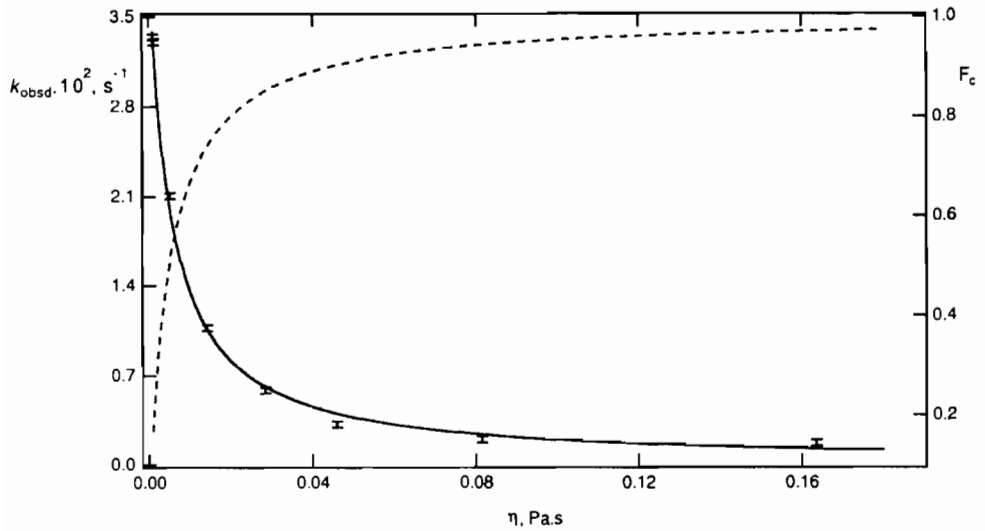

Fig. 1. Dependence of k_{obs} on viscosity (η) for the photolysis of $AdoB_{12}$ at 298 K, pH = 8.0. Error bar: standard deviation in k_{obs}. Solid line represents $\alpha_1/(1+\alpha_2\eta)$ vs. η. The values of α_1 and α_2 are given in Table 2. Dotted line: dependence of the fractional cage efficiency on viscosity (η) at 298 K.

TABLE 2. Parameters from fit of k_{obs} vs. viscosity (η) in $k_{obs} = \alpha_1/(1+\alpha_2\eta)$

Reaction	T (K)	α_1 (k_1) (s^{-1})	α_2 (k_c^0/Tk_d^0) ($Pa^{-1}\ s^{-1}\ K^{-1}$)
$AdoB_{12}$ photolysis	298.2	$(4.00 \pm 0.17) \times 10^{-2}$	191 ± 13
$AdoB_{12}$ photolysis	308.2	$(4.86 \pm 0.19) \times 10^{-2}$	236 ± 13
$AdoB_{12}$ photolysis	323.2	$(5.71 \pm 0.25) \times 10^{-2}$	335 ± 22
$AdoB_{12}$ thermolysis	380.6	$(2.58 \pm 0.10) \times 10^{-4}$	907 ± 62
$[AdoCbi]^+OH^-$ photolysis	298.2	$(7.74 \pm 0.09) \times 10^{-3}$	232 ± 15

chemically then the coenzyme. Exactly the same reduction is found on going to the cobinamide (5.6 ± 0.3). However, the α_2 values in Table 2 show the rate of recombination of the caged radical pair to be much less different. From the tabulated values the difference in free energy for the recombination reactions is: $\Delta\Delta G^{\ddagger} = 0.4$ kJ mol^{-1} ($\Delta G^{\ddagger} AdoB_{12} - \Delta G^{\ddagger}[AdoCbi]^+OH^-$) at 298 K. This result means

that the Gibbs function of the transition state for cage formation is nearly independent of the coordination of the axial base, so the transition state lies very close to the cage pair. This explains the fact that the volume of activation of k_1 is large: 20 $cm^3 mol^{-1}$ [5] reflecting the occupation of antibonding d orbitals and the resulting volume increase [5, 28]. A further consequence is that the contribution of the base-off form in eqn. (7) will be incorporated in k_{1t} without further effects.

Fractional cage efficiency

The difference in the barriers for cage recombination and escape is sometimes given by the fractional cage efficiency, F_c, defined as $F_c = k_c/(k_c + k_d)$ [10, 11]. Arguments have been presented [19], that for organometallic systems $F_c > 0.5$ may be more common then for organic systems. The photohomolysis work of Endicott and Netzel [9] has provided approximate values for k_c and k_d in aqueous solution at ambient temperatures, giving [11] $F_c = 0.7$ within a range of 0.2–1.0. F_c values may easily be calculated from our results. The calculated cage efficiency in water at 298 K is 0.2, which falls within the range found by the authors cited. As an illustration Fig. 1 gives the calculated values of F_c as a function of the solvent viscosity for aqueous solution at 298 K. The results also explain the fact that for thermal reactions at necessarily high temperatures $F_c \rightarrow 0$ is a good approximation [5]. Models for coenzyme B_{12} like cobaloximes and cosalens show a different behaviour [29, 30].

Temperature dependence

Koenig *et al.* have made it clear that the photochemical cage pairs in principle are not identical to their collisional counterparts, the difference being the additional momentum in the photochemical pair [13].

The fraction of the amount available for separation will depend on the possible competing routes. These include the ability of thermal disposal and the difference in escape and recombination rates between thermal and photochemical cage pairs. The difference in the latter two may be small because photolysis occurs by an absorption of a photon in the corrin ring of the coenzyme. The energy is then transmitted to the Co–C bond, possibly by electron transfer to the cobalt atom, resulting eventually in occupation of antibonding d orbitals and homolysis of the cobalt–carbon bond [31] This could mean that the excess energy remains in the ligand system and will not be used for extra separation of the radical pair. We have tentatively assumed the two pairs to be thermodynamically identical and tested $k_c^0 T/k_d^0$ for the three photochemical series at 298, 308 and 323 K and the thermal series at 381 K for obeyance of the Eyring equation. This procedure should be more reliable than the actual value of the constants in diffusion eqn. (6), as the classical study of Schuh and Fischer [32] has shown that, in spite of the fact that in general experimental values are higher than predicted, diffusion rates still depend linearly on T/η as expected from the Smoluchowski–Stokes–Einstein equation. This means that for the present analysis the deviation from the diffusion equation will only show up in the entropy of activation. As shown in Fig. 2 the fit is very good over this large temperature range, giving $\Delta H^{\ddagger}_c$ for the 'pure' recombination k_c^0 as 17.9 ± 0.3 kJ mol^{-1}. To the best of our knowledge this is the first time that an approximate value for the enthalpy of activation for the cage recombination reaction of a cobalamin has been derived. The value is in the range of activation enthalpies for diffusion controlled reactions [23]. It is now possible to get an indication of $\Delta S^{\ddagger}_c$ from the temperature dependence of k_c^0, based on the diffusion model. This results in $\Delta S^{\ddagger}_c = -21$ J K^{-1} M^{-1}. This value indeed is small and negative, as expected [11].

Bond dissociation energy (BDE)

If differential solvation effects are ignored [11], the bond dissociation energy (*BDE*) for the cobalt–carbon bond in coenzyme B_{12} is given by:

$$BDE = \Delta H^{\ddagger}_1 - \Delta H^{\ddagger}_c \approx \Delta H^{\ddagger}_{obs} + (1 - F_c)(\Delta H^{\ddagger}_d - \Delta H^{\ddagger}_c) - \Delta H^{\ddagger}_{-1} \quad (9)$$

There are various ways in which this general relationship can be simplified [11]. For instance, by neglecting $\Delta H^{\ddagger}_c$ and setting $\Delta H^{\ddagger}_d$ equal to $\Delta H^{\ddagger}_{-1}$, eqn. (9) is converted to

$$BDE \approx \Delta H^{\ddagger}_{obs} - F_c \Delta H^{\ddagger}_d \quad (10)$$

A further useful approximation [11] is to equate $\Delta H^{\ddagger}_d$ to the activation enthalpy for viscous flow ($\Delta H^{\ddagger}_\eta$) and assume a very efficient cage ($F_c = 1$). Equation (10) then becomes

$$BDE \approx \Delta H^{\ddagger}_{obs} - \Delta H^{\ddagger}_\eta \quad (11)$$

This is, in essence, the equation used by Halpern and co-workers [6, 33, 34] to determine the *BDE*. As stated before [11], a key variable in the *BDE* analysis is F_c. If F_c is known, then k_1 is obtained from k_{obs}:

$$k_1 = k_{obs}/(1 - F_c) \quad (12)$$

Having both F_c and k_{obs} and consequently k_1 as a function of temperature allows a direct determination of $(\Delta H^{\ddagger}_d - \Delta H^{\ddagger}_c)$ as well as $\Delta H^{\ddagger}_{-1}$. This would

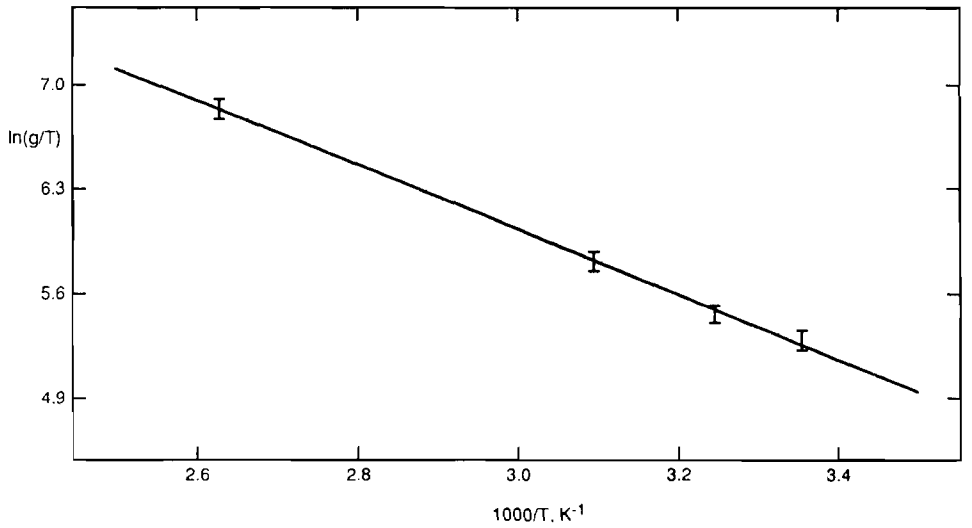

Fig. 2. Eyring plot for $g = \alpha_2 T$. Error bar: standard deviation calculated from Table 2. The solid line is the calculated value from the computerfit of $\alpha_2 T$ to the Eyring equation resulting in $\Delta H^{\ddagger}_c = 17.9$ kJ mol^{-1}.

valuably increase the understanding of the cage effect [11]. Using the results presented here, this is now possible.

Over the temperature range used for the thermolysis by Hay and Finke (358–383 K) [7], F_c does not vary much ($0.20 > F_c > 0.18$ as calculated from our results). This means that $\Delta H^{\ddagger}_d - \Delta H^{\ddagger}_c$ will be small. Also $\Delta H^{\ddagger}_1$ will be nearly equal to $\Delta H^{\ddagger}_{obs}$. A more accurate determination is possible from our approach using different solvent viscosities. Here $\Delta H^{\ddagger}_d - \Delta H^{\ddagger}_c$ results from the temperature dependence of $k_c/k_d = \alpha_2 \eta(T)$. This results in $\Delta H^{\ddagger}_d - \Delta H^{\ddagger}_c = -1.0 \pm 0.8$ kJ mol^{-1}. Consequently eqn. (11) is a very good approximation for the present case. Using the exact eqn. (9), after correction for the pre-equilibrium [19], the *BDE* for the base-on Co–C bond in $AdoB_{12}$ equals $\Delta H^{\ddagger}_1 - \Delta H^{\ddagger}_c = 136.6 - 17.9 = 119 \pm 8$ kJ mol^{-1}. It can thus be concluded that both the approximations used by Halpern (giving $BDE = 111 \pm 8$ kJ mol^{-1}) and Finke (resulting in $BDE = 125 \pm 8$ kJ mol^{-1}) are correct within the experimental error. As demonstrated by Brown and Peck-Siler [35], this large error is mainly due to the uncertainty in the base-on/base-off pre-equilibrium.

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