The Chemistry of Vitamin B_{12}. Part 23.[1] Decomposition of the Cobalt(I) Cobalamin B_{12s} in Aqueous Solution; a Novel Oscillating Reaction

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The decomposition of *ca.* 3×10^{-5} mol dm^{-3} aqueous solutions of the cobalt(I) (B_{12s}) to the cobalt(II) (B_{12r}) cobalamin under nitrogen has been studied at 36 °C by u.v.–visible spectrophotometry. The reaction shows marked oscillations in the relative concentrations of the cobalt(I) and cobalt(II) complexes with good isosbestic points and no evidence for the occurrence of any spectroscopically distinct intermediate. The oscillations appear to consist of a basic train with a period of 4—5 min and one or more superimposed trains. The oscillations are destroyed by light and the period decreases with increasing temperature, but the reaction is relatively unaffected by other variables such as pH (2—12).

Aqueous solutions of the cobalt(I) cobalamin B_{12s} are very sensitive to O_2,[2] but in the absence of O_2 decompose according to equation (1).[3,4] The kinetics of this decomposition have

$$Co^{I} + H_2O \longrightarrow Co^{II} + HO^- + \tfrac{1}{2}H_2 \qquad (1)$$

previously been studied indirectly by electrochemical techniques.[3-6] We have now studied this reaction directly by u.v.–visible spectrophotometry and observe the same rate *provided* the solution is exposed to normal daylight; if, however, the curvette is kept inside the spectrophotometer, the reaction becomes slower and striking oscillations are observed.

Oscillating reactions are observed in phenomena as diverse as periodicity in physiological processes and instability in chemical engineering processes; in the metalloenzyme field oscillations are shown by peroxidases and by mitochondria.[7] There has been increasing interest over the last decade in trying to understand their thermodynamic and kinetic basis, but few suitable model reactions are available for detailed study.[7-11] All known isothermal chemical oscillators operating in homogeneous solution are, in fact, based on reactions involving oxyhalogen ions (bromate, iodate, or chlorite).[12] The present reaction is, therefore, of interest as a new oscillating reaction with several unusual features and also of possible relevance to the role of the protein in certain B_{12}-dependent enzymes (see Discussion section). The aim of this paper is to report the conditions for, and the main features of, this oscillating reaction. We hope to report additional tests and to speculate on the mechanism in a later paper.

The main experimental problem involved in the direct spectrophotometric study of any reaction of B_{12s} is to produce a solution of B_{12s} as rapidly as possible, *i.e.* before reaction (1) has proceeded to any significant extent, and in the absence of excess of reducing agent, which would complicate the kinetics by reducing Co^{II} back to Co^{I} and might also introduce additional pathways for the decomposition of B_{12s}. It is known that ethylcobalamin undergoes photolysis mainly according to equation (2).[13-15] We find that cyclohexylcobalamin is also

$$Co{-}CH_2CH_3 \longrightarrow Co^{I} + CH_2{=}CH_2 + H^+ \qquad (2)$$

photolysed to give high yields of Co^{I} and that the rate of photolysis under our conditions is 2—3 times greater than that of ethylcobalamin; the formation of cyclohexene as the other product has already been reported.[16] We have therefore used the rapid (≤ 1 min) photolysis of cyclohexylcobalamin inside a spectrophotometer cell with fairly intense irradiation as our standard method of preparing B_{12s}.

Experimental

Materials.—A sample of aquocobalamin (vitamin B_{12a}) was kindly given by Mr. A. P. Domleo of Glaxo-Allenbury (Pty) Ltd. Nitrogen (Afrox, Germiston, Transvaal) was purified by passage through a vanadium(II) solution.[17] Ethyl bromide (Hopkins and Williams), cyclohexyl bromide (Emanuel), zinc dust (Hopkin and Williams, AnalaR reagent), NH_4Cl (Saarchem, Muldersdrift, Transvaal), ethylenediaminetetraacetic acid (H_4edta) sodium salt (BDH AnalaR reagent), and hydrogen (Afrox) were used without further purification. The following buffers, *etc.* were used: pH 1, 0.1N H_2SO_4; pH 1.6, 0.06N H_2SO_4; pH 2.1, 0.01N H_2SO_4; pH 2.8, 0.1 mol dm^{-3} acetic acid; pH 5.0, sodium acetate ($I = 0.2$ mol dm^{-3}); pH 7.0, sodium phosphate ($I = 0.2$ mol dm^{-3}); pH 9.2 and 11.0, both sodium carbonate ($I = 0.2$ mol dm^{-3}); pH 12.1, 0.02 mol dm^{-3} NaOH. The pH was checked with a Metrohm combined glass electrode, standardised with BDH buffers of pH 4.0, 7.0, and 10.0.

Preparation of Alkylcobalamins.—Ethylcobalamin was prepared as described.[18,19] We have previously prepared solutions of the unstable cyclohexylcobalamin by method (*a*) of ref. 20. This involves the addition of $Co(NO_3)_2$ which reacts with $NaBH_4$ to form black specks of insoluble Co_2B, which catalyse the reduction of aquocobalamin by $NaBH_4$. We now find that the photolysis under nitrogen of such a solution, which has not been freed from the catalyst, gives Co^{II} with little or no Co^{I}. If, however, the solution is freed from inorganic impurities by phenol–chloroform extraction [method (*b*) of ref. 20], then subsequent photolysis gives high yields of Co^{I}.

Cyclohexylcobalamin was therefore prepared by a method analogous to (*b*), using 10^{-5} mol dm^{-3} $Co(NO_3)_2$, leaving the reaction mixture (of B_{12s} and cyclohexyl bromide) to stand for *ca.* 30 min under nitrogen before extraction in air into the organic phase and then back into an aqueous solution of pH 2—3, in which the cobalamin can be stored until required as the stable protonated 'base-off' form.[21,22] The use of method (*b*) does, however, lead to the presence of a larger (5—10%) amount of B_{12a} in the solution of the cyclohexylcobalamin.

Preparation of the Cobalt(I) Vitamin B_{12s}.—(*i*) *From alkylcobalamins.* A solution of cyclohexylcobalamin (3.0×10^{-5} mol dm^{-3}, 2.2 cm^3) in the desired buffer solution was placed in a spectrophotometer cell, which was closed with a rubber septum, and deoxygenated with a brisk stream of N_2 for 10

min (*via* syringe needles inserted through the septum). The solution was then photolysed for 40—60 s with a 150-W tungsten lamp at a distance of 5 cm with the cell immersed in a beaker of cold water. This period was sufficient to ensure complete photolysis of the alkylcobalamin with only partial (unusually *ca.* 30%) conversion of Co^{I} into Co^{II}, which is also accelerated by light (see Results section). The cobalt(III) aquocobalamin present in the sample of cyclohexylcobalamin (see above) is immediately reduced by Co^{I} to give Co^{II}.[2] Any leak of O_2 into the cell could readily be detected by an increase in the amount of Co^{II} observed. Ethylcobalamin was photolysed to Co^{I} in the same way, but required a longer time (120 s).

(*ii*) *From aquocobalamin* (B_{12a}). Zinc dust (50 mg) was added to a solution of B_{12a} (3×10^{-5} mol dm^{-3}, 3 cm^3) in 10% aqueous NH_4Cl;[2] the suspension was deoxygenated and then filtered through a sintered glass directly into a spectrophotometer cell, which was closed with a rubber septum. All these operations were carried out in a glove-bag in an atmosphere of nitrogen. A small amount of very fine zinc always passed through the filter and gradually settled out on the bottom of the cell; even immediately after filtering, the amount was not sufficient to prevent qualitative studies of the spectrum in the 300—500 nm region.

U.v.–Visible Spectra.—Spectra were recorded on a JASCO Uvidec-1 spectrophotometer using 1-cm quartz cells which, unless otherwise stated, were thermostatted at 36 °C (approximately the lowest temperature for observing distinct, sustained oscillations). The concentration of the alkylcobalamins was calculated after their conversion into dicyanocobalamin (by photolysis in the presence of air and the addition of cyanide), using $\varepsilon_{367} = 3.04 \times 10^4$ dm^3 mol^{-1} cm^{-1}.[2] The concentrations of Co^{I} and Co^{II} were calculated using $\varepsilon_{387} = 2.80 \times 10^4$ and $\varepsilon_{473} = 0.92 \times 10^4$ dm^3 mol^{-1} cm^{-1} respectively.[2] To coat the inside surfaces of a cell with silicone, sufficient Dow silicone oil SE 30 was dissolved in chloroform to give a solution which, as the solvent evaporated, had the correct viscosity to be spread evenly on the surfaces with the help of a spatula and, on further evaporation, formed a clear skin which enabled one to check visually for complete coverage of the surfaces.

Results

Unless otherwise stated, the following ' standard ' conditions have been used for preparing solutions of Co^{I} and for studying their decomposition: 2 cm^3 of a *ca.* 3×10^{-5} mol dm^{-3} (total cobalt) solution of Co^{I} (*i.e.* with some Co^{II}) was prepared by the photolysis of cyclohexylcobalamin at pH 7 and $I = 0.2$ mol dm^{-3} and then studied by spectrophotometry at 36 °C under nitrogen in a 1-cm quartz cell using a slit width of 2.0 nm.

The spectrum immediately after photolysis of the cyclohexylcobalamin always shows the presence of *ca.* 30% Co^{II} due to photolysis of Co^{I} and/or reaction with traces of O_2; the final spectrum (see Figure 1) corresponds to complete (100 ± 5%) conversion of the initial cyclohexylcobalamin into Co^{II}. The repetitive scans (see Figure 1) show reasonable isosbestic points at *ca.* 308, 348, 420, and 550 nm throughout the reaction. The kinetic traces at 387 nm (see Figures 2 and 3) show well defined oscillations with considerable fine structure. The observed pattern of oscillations is variable, even in repeat experiments under apparently identical conditions [*cf.*

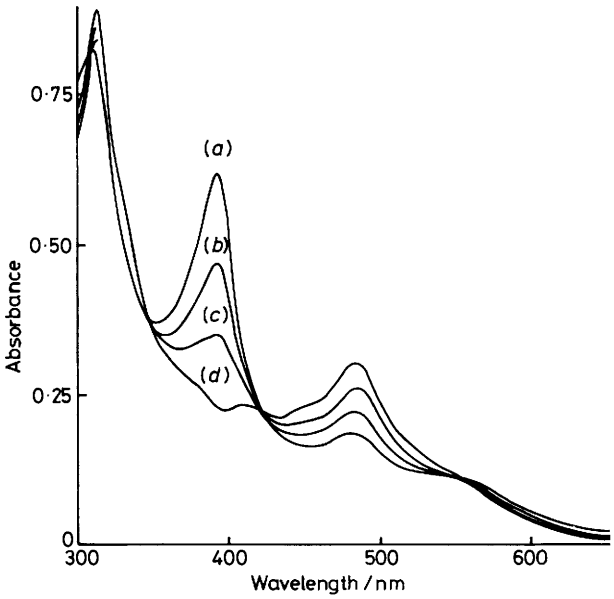

Figure 1. U.v.–visible spectra observed during the decomposition of Co^{I} to Co^{II} at various times (after the end of photolysis): (*a*) 0.5, (*b*) 49, (*c*) 115, and (*d*) 180 min. Conditions: 3.9×10^{-5} mol dm^{-3} Co, pH 7.0, and 36 °C

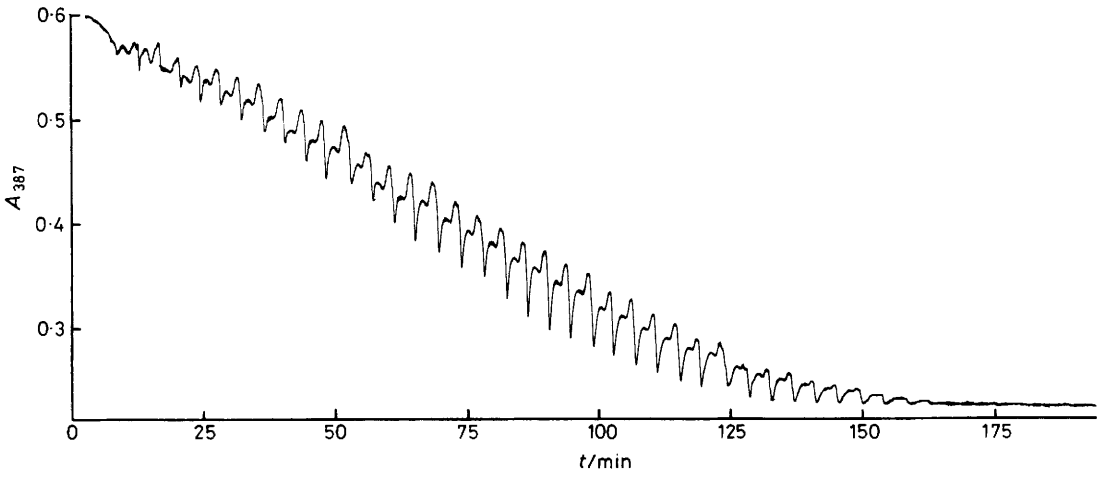

Figure 2. Changes in A_{387} observed during the decomposition of Co^{I} to Co^{II}; t_0 corresponds to the end of photolysis. Conditions: 3.0×10^{-5} mol dm^{-3} Co, pH 7.0, and 36 °C

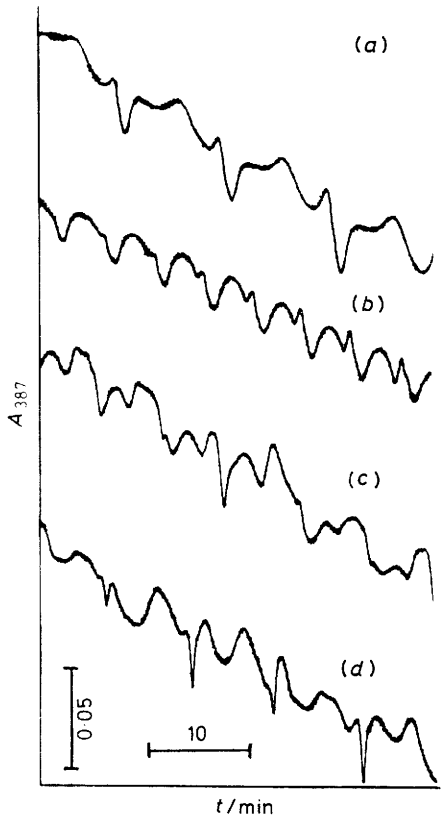

Figure 3. Other examples of changes in A_{387} with time, all for the period 33—73 min after the end of photolysis. Conditions: all 3.0×10^{-5} mol dm^{-3} Co; 36 °C; and pH 2.8 (*a*), 5.0 (*b*), 7.0 (*c*), and 12.1 (*d*)

Figures 2 and 3(*c*)], but appears to include a basic train of oscillations with a period of 4—5 min and one or more additional trains superimposed on the first. Kinetic traces at different wavelengths show that the amplitude of the oscillations varies with the wavelength (in nm) as follows: 377 < 387 > 397 > 407 > 420 (no oscillations or change in optical density at all) < 444 < 453 < 463 < 473 > 483 > 493, *i.e.* maximum amplitude is observed at the maxima of the cobalt(I) (387 nm) and cobalt(II) (473 nm) complexes and no change at the isosbestic point (420 nm). The amplitude of the oscillations may reach *ca.* 15% of the total cobalt (see Figure 2).

Neglecting the superimposed oscillations and the experiments at pH < 3 (see below), the underlying shape of the kinetic trace was usually sigmoidal with $t_{\frac{1}{2}} \approx 50$ min (see Figure 2) and sometimes linear (*i.e.* zero order) over the first half; the reaction clearly cannot be analysed according to simple first- or higher-order kinetics. Most of the kinetic traces also suggest that the superimposed oscillations build up in an autocatalytic manner at the start of the reaction, *i.e.* after formation of the B_{12s} by photolysis; this is probably associated with the fact that light ' kills ' the oscillations (see below). The use of solutions of B_{12s} which were prepared by the reduction of B_{12a} and contained traces of zinc dust to reduce the Co^{II} back to Co^{I} (see Experimental section) showed that oscillations could be maintained with an unchanged basic period of 5—5.5 min for over 30 h.

If an oscillating solution is photolysed for 5 s (under the conditions used for the photolysis of cyclohexylcobalamin), there is an immediate increase in the amount of Co^{I} decomposed to Co^{II}, followed by a period of 15—20 min of slow reaction with little or no oscillation before the rate increases

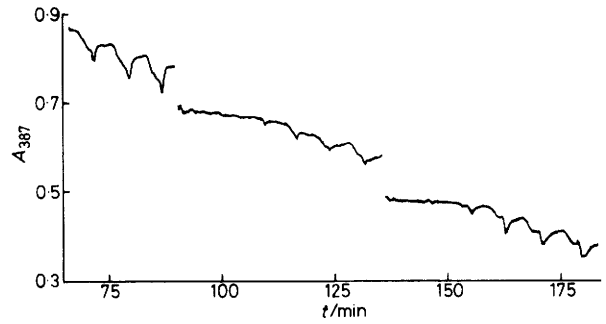

Figure 4. Effect of two 5-s periods of photolysis (at $t = 90$ and 135 min) on an oscillating reaction. Conditions: 4.6×10^{-5} mol dm^{-3} Co, pH 7.0, and 36 °C

and the oscillations build up again with the same period (see Figure 4). Repetitive scans showed no shift in the position of the isosbestic points after photolysis and the decrease in concentration of Co^{I} caused by photolysis agreed within experimental error with the increase in concentration of Co^{II}.

Tackett *et al.*[3] reported that the decomposition of B_{12s} in 0.025 mol dm^{-3} phosphate buffer of pH 6.9 at 25 °C occurred with a pseudo-first-order rate constant of log (k/min^{-1}) = −1.51. We also found that when a 5.4×10^{-5} mol dm^{-3} (total cobalt) solution of B_{12s} in phosphate buffer of pH 7.0 and I = 0.2 mol dm^{-3} at 25 °C was allowed to decompose in daylight on the bench, the reaction followed first-order kinetics for three half-lives to give a pseudo-first order rate constant of 0.031 min^{-1} (*i.e.* log k = −1.51) and $t_{\frac{1}{2}}$ = 22 min, in complete agreement with the previously reported results.

The effect of different variables on the basic (4—5 min) period of oscillations is summarised in the Table; the ' standard ' conditions have been given above. The following notes refer to particular experiments, numbered as in the Table. (2) The range of concentration studied was limited by the need to follow changes in optical density in the 300—550 nm region (which includes well defined maxima of all the various likely corrinoids, as well as several isosbestic points) in a 1-cm cell (to minimise the problems of reaction with O_2); we hope to be able to extend the range of concentration studied in later experiments. (4) The kinetic trace at pH 2.8 did not exhibit the sigmoidal or zero-order character (see above) observed at higher pH. Further lowering of the pH caused an increase in the amount of Co^{I} decomposed during the period of photolysis; oscillations could still be detected at pH 1.6 but not at pH 1.0. This change is obviously associated with the reported protonation of B_{12s} with pK = 1, which probably forms the cobalt(III) hydride complex.[23] (6) Lowering the temperature (to 25 and 14 °C) appears to increase the period, but the pattern of oscillations becomes much less distinct and regular. (7) The possible role of H_2 in any reversible step in the decomposition of Co^{I} was tested at high pH because the reducing power of H_2 relative to the Co^{I}–Co^{II} couple increases with pH [*cf.* equation (1)]. (9) Varying the slit width was used to test whether the low level of light intensity within the spectrophotometer served to promote or inhibit the reaction. The data in the Table show that none of these variables except temperature has any significant effect on the period of oscillation, although the use of reduction as the method of preparing Co^{I} seems to give a consistently longer period (5—5.5 min) than photolysis (4—5 min). Raising the temperature also affects the kinetics of the background reaction (*i.e.* neglecting the superimposed oscillations) such that at 79 °C the reaction follows first-order kinetics for over four half-lives with $t_{\frac{1}{2}}$ = 27 min.

Table. Effect of experimental variables on the basic period of oscillation

Experiment	Variable	Conditions	Period (min)	Notes
1		(' standard ')	4—5	
2	[Co]	9.6×10^{-5} mol dm^{-3}	4	see text
		2.8×10^{-4} mol dm^{-3}	4.5	see text
3	Preparation of Co^{I}	photolysis of ethylcobalamin	4.5	see Experimental section
		B_{12a} + zinc dust	5.5	see Experimental section
4	pH	pH 1.0	—	see text
		1.6	3	see text
		2.1	4	see text
		2.8	5	see Figure 3(*a*)
		5.0	5	see Figure 3(*b*)
		7.0	4	see Figure 2
		9.2	4	
		11.2	4.5	
		12.1	4	see Figure 3(*d*)
5	Ionic strength	deionised water, pH 8, $I \approx 0$	5	
6	Temperature	14 and 25 °C	—	see text
		36 °C	4	
		50 °C	2	
		79 °C	1	
7	Gas phase	H_2 (pH 12.1)	4	see text
8	Cell surface	silicone-coated (B_{12s} from B_{12a} + zinc)	5.5	see Experimental section
9	Slit width	0.5 nm	3.5	see text

We attempted to test for the possible role of transition-metal ions by examining the effect of H_4edta. The presence of 3×10^{-5} mol dm^{-3} H_4edta at pH 7 had no significant effect on the period of the oscillations (3.5 min), but higher concentrations accelerated the rate of decomposition.

Discussion

Our results show that the reported kinetics of decomposition of B_{12s} in aqueous solution, which were obtained by electrochemical techniques without explicit provision for excluding light,[3] include a light-promoted reaction. The ' dark ' reactions are slower and can show remarkable oscillations (see Figures 2 and 3), which have not previously been reported. The oscillations can be ' killed ' by light and the rate of decomposition becomes very slow immediately after a ' killed ' solution is placed in the dark, but the rate and oscillations both build up again to previous levels (Figure 4). There are, therefore, at least three types of reaction which may be observed for the decomposition of B_{12s}, *viz.* a photochemical reaction, an oscillating dark reaction, and a very much slower, probably non-oscillating, dark reaction. The oscillatory reaction is essentially pH-independent over the range of pH 2—12, while the ' bench-top ' reaction shows [3] a very complex dependence on pH which may, in the light of present results, reflect the occurrence of various parallel reactions, both thermal and photochemical.

The oscillatory reaction involves the virtually stoicheiometric conversion of Co^{I} into one or more (see below) cobalt(II) complexes. Since we have not yet confirmed the occurrence of oscillations at the cobalt concentrations required for preparing a sufficient amount of H_2 for analysis, we do not know whether the dark reaction obeys equation (1) or not. The main features of this reaction can be summarised as follows.

(*a*) The oscillatory reaction occurs in homogeneous solution (no effect of coating the cell surface with silicone, see Table), appears to require no reagent other than the starting material (B_{12s}) and the solvent (water), and can be maintained for over 30 h with a virtually unchanged period of oscillation in the presence of a slight amount of zinc dust to regenerate the Co^{I}. Attempts to test for the possible role of trace metal ions by examining the effect of H_4edta showed that H_4edta itself accelerated the decomposition of Co^{I} to Co^{II} (compare the observations of Das [4]) and were therefore inconclusive. Since, however, we observed the same oscillations whether the Co^{I} was prepared from aquocobalamin directly by reduction with zinc or indirectly *via* a multi-step synthesis and purification of an alkylcobalamin, we conclude that trace metals are not required.

(*b*) The kinetic traces appear always to include a basic train of oscillations with a period of 4—5 min, together with one or two additional trains superimposed on the first (see Figures 2 and 3). The degree of fine structure, caused by the several trains and their different relative amplitudes, appears to be greater than that reported for any other simple homogeneous system in solution; compare, for example, the oscillations shown in refs. 7 and 12. It is therefore not surprising that the oscillations show considerable variation, even in duplicate experiments under identical conditions.

(*c*) There is no evidence for the formation of any intermediates with spectra significantly different from those of the initial cobalt(I) and final cobalt(II) corrinoids. However, since the total concentrations of Co^{I} and Co^{II} are oscillating and since the concentrations of the starting materials cannot oscillate,[10] we conclude that other cobalt(I) and probably also cobalt(II) intermediates with modified side-chains but almost identical spectra are involved. It is well established that the spectra of cobalt corrinoids are very sensitive to changes involving the Co atom or the conjugated corrin ring but relatively insensitive to changes involving the side-chains.[2]

(*d*) The 4—5 min period of the basic train of oscillations is decreased by raising the temperature, but changes in pH (2—12), cobalt concentration, ionic strength, and the gaseous atmosphere have virtually no effect on the period of oscillations (Table) or on the approximate half-life of the reaction.

We do not wish to speculate here on the possible mechanism of reaction except to point out that the occurrence of oscillations depends on co-operative interaction between two or more ' species ', which could be either different corrinoid

molecules or different sites within the same corrinoid molecule. The absence of any marked dependence of the period on the cobalt concentration does, in fact, support the latter, but the results are not conclusive. We hope to obtain further evidence on the possible role of the side-chains.

The formation of B_{12s} has been observed spectroscopically in one of the methyl-transfer enzymes (methionine synthetase) [24] and it may also play a role in the isomerase reactions.[25] Our observation that the reaction of protein-free B_{12s} with the solvent is an oscillating reaction and that the reaction is even slower after the oscillations have been killed by light (Figure 4) implies that the protein can stabilise B_{12s} towards this reaction by preventing interaction with a second molecule of B_{12s} and/or with the essential functional groups of the side-chains. Compare the analogous situation with the cobalt(II) cobalamin B_{12r}, where studies on the reaction of protein-free B_{12r} with O_2 showed that the protein could stabilise B_{12r} towards irreversible oxidation by preventing interaction with a second molecule of B_{12r} or with amino acids containing reducing groups such as tyrosine and cysteine.[26]

The oscillating reaction described here offers several advantages as a model reaction for investigating the basis of oscillatory behaviour; it occurs in solution, is easy to study (by u.v.–visible spectrophotometry), is robust (oscillations are observed over a wide range of conditions), and does not require careful control of reagent concentrations (since only one reagent is involved). The main disadvantage is the difficulty of preparing and handling the very oxygen-sensitive cobalt(I) corrinoid. The most interesting features, however, are that the key oscillating intermediates appear to be present in unusually high concentration (the amplitude of the oscillations may reach 15% of the total cobalt) and that a large amount of information is potentially available through analysis of the fine structure of the oscillations. This also appears to be the first reported oscillatory reaction in solution which does not involve an oxyhalogen anion (*cf.* ref. 12).

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