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PHOTOLYSIS OF HYDROPHOBIC VITAMIN B_{12} DERIVATIVES WITH ALKYL LIGANDS IN NONAQUEOUS MEDIA

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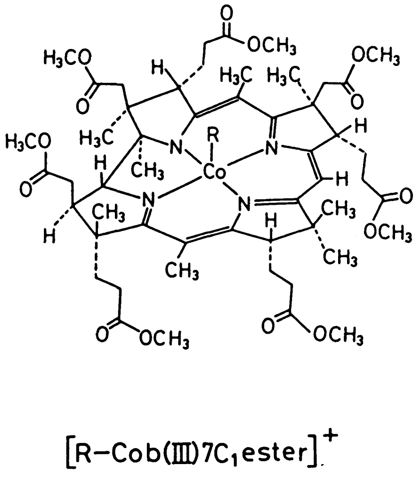
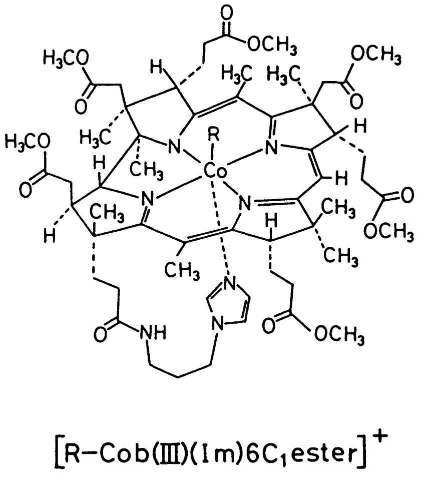
Aerobic photolysis of hydrophobic vitamin B_{12} derivatives having alkyl ligands was enhanced as the solvent polarity was reduced and by the coordination of a proximal base placed within the hydrophobic complexes. The quantum yield remained constant regardless of the irradiation wavelength.

We have been investigating the reactivity of hydrophobic vitamin B_{12} derivatives in which the peripheral amide moieties of the naturally occurring vitamin B_{12} are replaced with carboxylic ester groups. These modified cobalt complexes are soluble in organic solvents of a wide polarity range and may be utilized as homogeneous catalysts in such media.[1)] Alkylated complexes of vitamin B_{12} derivatives are photosensitive and undergo cleavage of the cobalt-carbon bond upon irradiation with the visible light.[2)] We have previously carried out the alkylation reactions of three hydrophobic vitamin B_{12} species in the Co^{I} state with alkyl bromides to afford $[R\text{-}Cob(III)7C_1ester]^+$, $[R\text{-}Cob(III)(Im)6C_1ester]^+$, and $[R\text{-}Cob(III)(Im{:}cap)\text{-}5C_1ester]^+$ and examined the coordination effect of proximal bases placed in the complexes on the reactions.[3)] In this communication, we describe the photolysis of the three different types of alkylated vitamin B_{12} derivatives cited above and discuss the kinetic effects of solvent nature and intramolecular axial bases on the reaction.

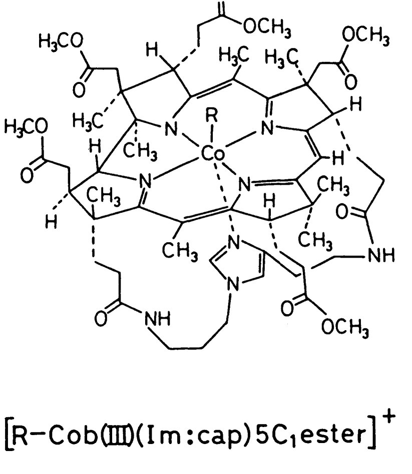
When heptamethyl methylaquacobyrinate perchlorate,[1a)] $[(CH_3)(H_2O)Cob(III)7C_1\text{-}$



$[R\text{-}Cob(III)7C_1ester]^+$



$[R\text{-}Cob(III)(Im)6C_1ester]^+$



$[R\text{-}Cob(III)(Im{:}cap)5C_1ester]^+$

ester]ClO_4, in dichloromethane was irradiated with the visible light under aerobic conditions, the cobalt-carbon bond underwent cleavage, and the generated Co^{II} complex was rapidly oxidized to the corresponding Co^{III} species as shown in Fig. 1. Similar spectral changes were observed in other organic solvents. However, spectra observed in alcohols at the final stage were identical with that of the Co^{II} complex as typically shown in Fig. 2. Since alcohols are readily oxidized with Co^{III} species,$^{4)}$ the Co^{III} complex must be rapidly reconverted into the Co^{II} species in alcohols (refer to Eq. 1). Pseudo-first-order rate constants for the aerobic photolysis in various solvents except methanol were evaluated from the absorbance increase at 540 nm, while that in methanol was done from the absorbance decrease at 380 nm (Table 1). The reaction rate is presumably subjected to change by the following factors: (i) a cage effect as estimated by the solvent viscosity; (ii) solubility of dioxygen, a radical scavenger, in reaction media; (iii) the microenvironmental polarity of reaction media; (iv) the coordination affinity of solvent molecules for the cobalt complex. Since the rate constant becomes larger

$$[\text{R-Cob(III)7C}_1\text{ester}]^+ \xrightarrow{h\nu} [\text{Cob(II)7C}_1\text{ester}]^+ \xrightarrow{O_2}$$

$$[\text{Cob(III)7C}_1\text{ester}]^{2+} \xrightarrow{\text{alcohol}} [\text{Cob(II)7C}_1\text{ester}]^+ \qquad (1)$$

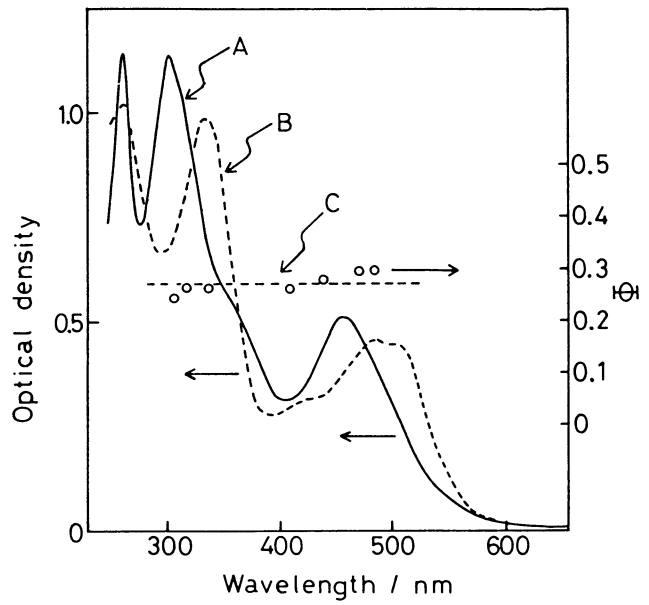


Fig. 1. Electronic spectral change and quantum yields for the aerobic photolysis of $[(CH_3)(H_2O)Cob(III)7C_1ester]ClO_4$ in dichloromethane at 20.5 ± 0.1 °C: A, $[(CH_3)(H_2O)Cob(III)7C_1ester]ClO_4$ (5.1×10^{-5} mol dm^{-3}); B, after irradiation with a 200-W tungsten lamp from a distance of 60 cm; C, average quantum yield (open circles represent experimental data).

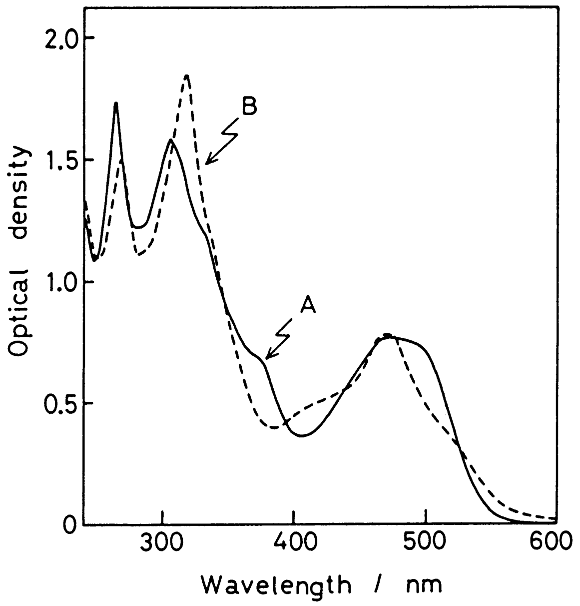


Fig. 2. Electronic spectral change for the aerobic photolysis of $[(CH_3)(H_2O)Cob(III)7C_1ester]ClO_4$ in methanol at 20.5 ± 0.1 °C: A, $[(CH_3)(H_2O)Cob(III)7C_1ester]ClO_4$ (6.7×10^{-5} mol dm^{-3}); B, after irradiation with a 200-W tungsten lamp from a distance of 60 cm.

Table 1. Pseudo-first-order rate constants for aerobic photolysis of $[(CH_3)(H_2O)Cob(III)7C_1ester]ClO_4$ at 20.5 ± 0.1 °C[a] and some related parameters

Medium	$E_T(30)$[b] / kcal mol^{-1}	$\eta \times 10^3$ [c] / N s m^{-2}	Solubility of O_2[d] (Ostwald)	$k_{obsd} \times 10^2$ / s^{-1}	k_{rel}[e]
H_2O	63.1	1.002 (20 °C)	0.023 (20 °C)	0.48	1.0
CH_3OH	55.5	0.597 (20 °C)	0.187 (18.5 °C)	0.86	1.8
DMF	43.8	0.924 (20 °C)		0.93	1.9
CH_3COCH_3	42.0	0.337 (15 °C)	0.222 (19 °C)	2.13	4.4
CH_2Cl_2	41.1	0.449 (15 °C)		1.69	3.5
$CH_3COOC_2H_5$	38.1	0.455 (20 °C)	0.175 (20 °C)	2.01	4.2
C_6H_6	34.5	0.652 (20 °C)	0.174 (19 °C)	2.70	5.6

a) $[(CH_3)(H_2O)Cob(III)7C_1ester]ClO_4$ (6.7×10^{-5} mol dm^{-3}) irradiated with a 200-W tungsten lamp from a distance of 60 cm. b) Solvent polarity parameter, see: C. Reichardt, "Solvent Effects in Organic Chemistry," Verlag Chemie, Weinheim (1979). c) Viscosity parameter, see: "CRC Handbook of Chemistry and Physics," 61st ed, ed by R. C. Weast, CRC Press, Boca Raton, Florida (1980), pp. F-52 – F-57. d) "Solubility of Inorganic and Metal Organic Compounds," ed by A. Seidell and W. F. Linke, American Chemical Society, Washington, D. C. (1965), Vol. 2, p. 1235. e) Relative rate; k_{obsd} in H_2O as a reference.

as the solvent polarity decreases, factor iii is the most prevailing one for acceleration of the aerobic photolysis.

The quantum yield (Φ) for the photolysis of $[(CH_3)(H_2O)Cob(III)7C_1ester]ClO_4$ was determined in dichloromethane under monochromatic irradiation with a 150-W xenon lamp; 302, 313, 334, 405, 436, 468, and 480 nm. The calculations of Φ values were based on the initial rate of photolysis (an absorbance increase at 540 nm; see Fig. 1) by using potassium ferrioxalate as a reference chemical actinometer.[5] The quantum yield remains nearly constant ($\Phi \cong 0.27$) regardless of the irradiation wavelength over the region covering the α-, β-, and γ-bands[6] (Fig. 1). This indicates that the photolysis is initiated by the absorption of a quantum of light corresponding to a π-π* transition localized within the conjugated corrin ring.[7]

In order to estimate the coordination effects provided by the intramolecular axial bases on the reaction, the aerobic photolyses of $[R\text{-}Cob(III)7C_1ester]^+$, $[R\text{-}Cob(III)(Im)6C_1ester]^+$, and $[R\text{-}Cob(III)(Im{:}cap)5C_1ester]^+$ were examined in various organic solvents. These alkylated complexes were synthesized by the reactions of the corresponding Co^I complexes with alkyl halides in reference to the method described previously.[3] The rate constants for the aerobic photolysis are listed in Table 2; the lower the solvent polarity is, the faster the rate becomes in a manner as mentioned above (vide supra). The presence of an intramolecular axial base resulted in enhancement of the photolysis rate, and the rate acceleration is larger for the capped hydrophobic vitamin B_{12}, $[R\text{-}Cob(III)(Im{:}cap)5C_1ester]^+$, than for the other one with a flexible axial base, $[R\text{-}Cob(III)(Im)6C_1ester]^+$. The enhancement must be originated from the coordination effects provided by the proximal bases: (i) the coordination of an intramolecular base to the nuclear cobalt induces some

Table 2. Pseudo-first-order rate constants for aerobic photolysis of hydrophobic vitamin B_{12} derivatives with alkyl ligands at 20.5 ± 0.1 °C[a)]

Alkyl moiety	Medium[b)]	$E_T(30)$	$k_{obsd} \times 10^2/s^{-1}$		
		kcal mol^{-1}	Complex 1[c)]	Complex 2[d)]	Complex 3[e)]
C_2H_5	CH_3OH	55.5	0.90	1.06	1.20
C_3H_7	CH_3OH	55.5	0.97	1.22	1.41
C_2H_5	C_2H_5OH	51.9	0.97	1.10	1.41
C_3H_7	C_2H_5OH	51.9	1.00	1.18	1.69
C_2H_5	n-PrOH	50.7	1.04	1.14	1.64
C_3H_7	n-PrOH	50.7	1.05	1.18	1.82
C_2H_5	DMSO	45.0	0.90	1.67	1.82
C_3H_7	DMSO	45.0	0.93	1.69	2.08
C_2H_5	CH_3COOCH_3	40.0	1.20	1.54	2.13
C_3H_7	CH_3COOCH_3	40.0	1.64	2.33	2.94

a) Alkylated hydrophobic vitamin B_{12}'s (2.1×10^{-5} mol dm^{-3}) irradiated with a 200-W tungsten lamp from a distance of 60 cm. b) Each solvent (3 mL) contains 150 μL of a methanol solution of NaOH (0.1 mol dm^{-3}). c) $[R\text{-Cob(III)}7C_1\text{ester}]^+$. d) $[R\text{-Cob(III)(Im)}6C_1\text{ester}]^+$. e) $[R\text{-Cob(III)(Im:cap)}5C_1\text{ester}]^+$.

deformation of the overall coordination geometry, so that the steric interaction between an alkyl ligand and the corrinoid skeleton becomes larger; (ii) the recombination of a free alkyl radical and the Co^{II} complex, generated by the photolysis, is significantly inhibited sicne the Co^{II} complex having an axial base is autoxidized to the Co^{III} species more readily than the one without any proximal base under aerobic conditions.[3)]

In conclusion, the coordination of an intramolecular base to the nuclear cobalt(III) of hydrophobic vitamin B_{12} analogues results in alteration of the electronic character of the cobalt atom and the overall coordination geometry. In this regard, the present vitamin B_{12} derivatives are expected to be utilized as homogeneous catalysts in organic media. Our studies are in progress along this line.

References

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