Anaerobic Photodecomposition of Alkylaquocobaloximes in Aqueous Solution

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The photochemical decomposition of alkylaquocobaloximes in aqueous solution under anaerobic conditions depends critically on the presence of acid. At pH 2, photoreaction is fast and wavelength-independent ($\phi > 0.1$ for several alkyl substituents) and involves the production of aqueous cobalt(II) ion and radical intermediates which yield products typical of abstraction and dimerisation reactions. At pH 7, photoreaction is *ca.* ten-fold less efficient to yield $[Co^{II}(Hdmg)_2(OH_2)_2]$ [Hdmg = dimethylglyoximate(1−)] together with an alk-1-ene derived from the axial alkyl ligand.

PRINCIPALLY due to their interest as model compounds for the vitamin B_{12} coenzyme, adenosylcobalamin (acob), the photochemistry of alkylcobaloximes [$Co^{III}R(Hdmg)_2L$] [R = alkyl, Hdmg = dimethylglyoximate(1−), L = axial Lewis-base ligand] and simple alkylcobalamins has been investigated by several groups and

extensively reviewed.[1-8] The course of acob-dependent enzymatic reactions, according to one scheme,[9,10] depends on the intermediacy of radicals in which the 1,2-shift supposed to be characteristic of acob-dependent processes can occur, *e.g.* that in the conversion of certain 1,2-diols into aldehydes.[4,10,11] Following the binding of acob to enzyme which splits its Co–C bond, the resulting adenosyl radical attacks substrate (*e.g.* $MeCHOHCH_2OH$) to produce a substrate-derived radical S$^{\bullet}$ (*e.g.* MeCHOH-$\dot{C}$HOH). The latter is converted into propionaldehyde *via* a product-related radical P$^{\bullet}$ [*e.g.* Me$\dot{C}$HCH(OH)$_2$]. Since the photohomolysis of the Co^{III}–C bond in the alkylcobaloximes and cobalamins should release alkyl radicals, these might be made to simulate the behaviour of either the 5′-deoxyadenosyl radical released by acob [10] in the enzymatic reactions or the radical intermediates between substrate and product.

The alkylcobaloximes are characterised by intense bands at *ca.* 380 and 440 nm assigned to charge-transfer transitions.[12] (The alkylcobalamins are rather similar although the band at 380 nm is only a shoulder on bands extending to below 300 nm.) Photolysis in the band at 440 nm of methylcobaloximes in anaerobic aqueous solution when L = pyridine, imidazole, or NH_3 is said to produce no change in the absorption spectrum,[12] implying a quantum yield of zero for photodestruction ($\phi_{dec.}$), although for *aerobic* solution with L = H_2O, $\phi_{dec.}$ reached [12] 5.4×10^{-4}. This apparent photostability of anaerobic aqueous solutions mirrors that reported for methylcobalamin by Pratt [13] who found nitrogen-flushed solutions to be *ca.* 1.2×10^3-fold more photostable than oxygen-flushed solutions; for the latter [14] $\phi_{dec.}$ (490 nm) $= 0.35 \pm 0.04$. This has prompted the suggestion by several workers that the primary act is that of formation of a caged radical-pair [equation (1)] which reverts to

$$[Co^{III}R(Hdmg)_2L] \overset{h\nu}{\rightleftharpoons} \{R^{\bullet} + [Co^{II}(Hdmg)_2L]\} \quad (1)$$

starting material with an efficiency of *ca.* 0.999, but which can be decomposed by additives such as O_2,[13] alcohols,[15] *p*-benzoquinone,[15] *etc.* R$^{\bullet}$ can also be spin-trapped [16] and some direct e.s.r. evidence of the role of radicals has been presented.[6] An acidity dependence of $\phi_{dec.}$ for several alkylcobalamins in aerated solution has been noted.[17] We report here: (*i*) that, for anaerobic aqueous solution, alkylaquocobaloximes are very photosensitive at moderate acidities (pH 1—5); (*ii*) photoreaction is much less efficient at pH 7 than at lower pH and gives a different cobalt-containing product; and (*iii*) the fate of the released axial alkyl group depends strongly on pH.

EXPERIMENTAL

Materials.—The salt $CoCl_2 \cdot 6H_2O$ and pyridine (AnalaR grade), dimethyl sulphide, potassium tetrahydroborate, and dimethylglyoxime (all reagent grade) were used without further purification. Benzyl bromide, 1-bromohexane, 1-bromopropane- and 2-bromopropane were redistilled before use. 1-Bromo-3-phenylpropane was prepared from 3-phenylpropan-1-ol and 48% aqueous HBr as a pale yellow liquid, b.p. 104—106 °C at 8 mmHg (lit.,[18] 109 °C at 11 mmHg).*

The alkylaquocobaloximes [$CoR(Hdmg)_2(OH_2)$] (R = Pr^n, Pr^i, n-C_6H_{13}, or $PhCH_2CH_2CH_2$) respectively were prepared by room-temperature hydrolysis of the corresponding dimethyl sulphide complexes.[19,20] For R = Me, Et, and $PhCH_2$, the aqua-complexes were obtained by hydrolysis of the corresponding pyridine complex [19] with $HClO_4$. Typically, [CoMe(Hdmg)$_2$(py)] (430 mg) was dissolved in CH_2Cl_2 (4 cm^3) and stirred for 2 h at room temperature with 1 mol dm^{-3} $HClO_4$ (5 cm^3) in a flask protected from light. The orange precipitate was then filtered on to a glass sinter and washed free from pyridinium perchlorate with portions (2 × 1 cm^3) of ice-cold water. The product, which was shown by ^{1}H n.m.r. (see later) to be a mixture of aquomethylcobaloxime and monoprotonated material, was recrystallised three times from distilled water to yield a pure sample of aquomethylcobaloxime as demonstrated by elemental analysis and ^{1}H n.m.r. (Tables 1 and 2). For R = Et and $PhCH_2$, a greater yield of alkylaquocobaloxime was obtained by substitution of CCl_4 for CH_2Cl_2 as the organic phase. For all the materials the yield was *ca.* 200 mg.

[$^2H_8$]Dimethylglyoxime was prepared by refluxing dimethylglyoxime (1.62 g) with 0.3 mol dm^{-3} DCl–D_2O (16.5 cm^3) for 24 h. The product was filtered off and washed with portions (2 × 1 cm^3) of ice-cold D_2O. The exchange was repeated twice more with 13.5 and 10.5 cm^3 of 0.3 mol dm^3 DCl. The product was finally dried *in vacuo* at room-temperature (yield of deuteriated material 0.84 g). Mass spectroscopic analysis (we thank P.C.M.U., Harwell, for this result) gave the following extent of deuteriation in the

* Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa.

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methyl groups: D_6, 36; D_5, 35; D_4, 19; D_3, 7; D_2, 2; D_1, 0.5; and D_0, 0.1%. Aquomethylcobaloxime deuteriated in the methyl groups of Hdmg and at the bridging hydroxyl groups was prepared directly from this material, using the standard method,[19] except that all the washings were with D_2O.

Methods.—Hydrogen-1 n.m.r. spectra were recorded on either Perkin-Elmer R12 (60 MHz) or Bruker WH90 (90 MHz) spectrometers. Visible absorption spectra of the cobaloximes were recorded on a Cary 14 spectrophotometer at room temperature using 5-cm³ cells with a sample concentration of *ca.* 2×10^{-4} mol dm^{-3}. Gas analyses were made, employing a Perkin-Elmer F11 gas chromatograph (F.I.D.) using 2-m × 2-mm columns with nitrogen as carrier gas. The lower hydrocarbons (C_1–C_3) were well separated on a phenyl isocyanate–Porasil C column (80—100 mesh) at room temperature, C_6 hydrocarbons using Chromosorb 101 (80—100 mesh) at 100 °C, and C_{12} hydrocarbons on 10% Apiezon L–Chromosorb P at 150 °C. For all the samples, injection volumes of 0.05 cm³ of the vapour above the photolysed reaction, produced from each cobaloxime (*ca.* 20 mg) dissolved in solvent (19.5 cm³), were adequate.

TABLE 1

Analytical data (%) [a] for $[CoR(Hdmg)_2(OH_2)]$

R	Found C	Found H	Found N	Calc. C	Calc. H	Calc. N
Me	33.6	5.85	17.7	33.55	5.95	17.4
Et	35.9	6.25	16.7	35.7	6.30	16.65
Pr^n	37.45	6.60	15.95	37.7	6.60	16.0
Pr^i	37.8	6.50	16.1	37.7	6.60	16.0
n-C_6H_{13}	42.85	7.45	14.25	42.85	7.45	14.3
$PhCH_2$ [b]	43.0	6.05	13.45	43.25	6.05	13.45
$Ph(CH_2)_3$	47.75	6.35	13.5	47.9	6.40	13.15

[a] Analyses by CHN Analysis Ltd., Wigston, Leicester. [b] Calculated for $[Co(CH_2Ph)(Hdmg)_2(OH_2)]\cdot H_2O$.

Solutions for irradiation were prepared by dissolving the cobaloxime (*ca.* 1—2 mg) in 25 cm³ of either $Na[ClO_4]$–$HClO_4$ (total $[ClO_4^-] = 0.2$ mol dm^{-3}, pH 2.00) or doubly distilled water (pH 7). [The use of triply distilled water in some runs (doubly distilled redistilled from alkaline permanganate) made no difference to the quantum yields.)] All the operations were carried out in a darkened room. For the intermediate pH range, phthalate buffers were employed. The solutions were freed from dissolved oxygen by bubbling with a stream of argon for an optimum time of 30 min. The argon had been prewashed with acidic chromium(II) solution, 2 mol dm^{-3} Na[OH], and then passed through two bottles containing solvent (as used in the photolysis solution) to presaturate the vapour.

TABLE 2

60-MHz Proton shifts of alkylaquocobaloximes

R	δ/p.p.m., *J*/Hz
Me	0.67 (s), CH_3; 2.18 (s), Hdmg CH_3
Et	0.05 (t), *J* 8.0, CH_3; 1.66 (q), *J* 7.5, CH_2; 2.13 (s), Hdmg CH_3
Pr^n	0.73 (m), CH_3CH_2; 1.59 (m) CH_2; 2.21 (s), Hdmg CH_3
Pr^i	0.18 (d), *J* 6.5, CH_3CCH_3; *ca.* 1.9 (m), CH; 2.21 (s), Hdmg CH_3
n-C_6H_{13}	0.79 (s), 0.91 (s), 1.12 (s), 1.45 (s), 1.60 (s), 1.74 (s), all C_6H_{13}; 2.16 (s), Hdmg CH_3
$PhCH_2$	2.17 (s), Hdmg CH_3; 2.79 (s), CH_2; 7.00 (s), 6.95 (s), 6.92 (s), C_6H_5
$Ph(CH_2)_3$	*ca.* 1.5 (m), $2CH_2$; 2.17 (s), Hdmg CH_3; 2.41 (t), *J* 6.5, CH_2; 7.08 (d), *J* 2.5, C_6H_5

Quantitative analysis of the organic products produced by photolyses of $[Co(CH_2CH_2CH_2Ph)(Hdmg)_2(OH_2)]$ at both pH 2 and pH 7 was effected by using a Waters Associates model 6000A high-pressure liquid chromatograph fitted with a model 440 absorbance detector operating at 254 nm. The cobaloxime (25 mg) was dissolved in solvent (50 cm³) and the solutions were photolysed. The organic products were extracted with portions (3 × 1 cm³) of spectroscopic hexane and the extracts were made up to 5 cm³. Samples (5—25 μl) were injected, and effective separation of the components was obtained using a flow scale of 1 cm³ min^{-1} hexane on a μ Porasil column. In a separate experiment, standard solutions of propylbenzene, allylbenzene, and 1,6-diphenylhexane were used to calibrate the detector. Authentic 1,6-diphenylhexane was prepared by hydrogenation (Pd/C/H_2) of 1,6-diphenylhexa-1,3,5-triene (Aldrich).

Measurement of the K *for protonation of aquomethylcobaloxime.* The proton-association constant K_1 for unprotonated aquomethylcobaloxime, B, expressed in terms of equilibrium concentrations, was determined by utilising the differential proton shifts of the axial CH_3 in the protonated, $[HB]^+$, and unprotonated forms. Under these conditions of fast exchange on the n.m.r. time scale, the observed shift, $\delta_{obs.}$, in solutions containing $[CoMe(Hdmg)_2(OH_2)]$ and acid is a weighted average of those in the fully protonated (δ_1) and unprotonated (δ_0) forms [equation (3)]. Thus a series of 23

$$K_1 = \frac{[HB^+]}{[B][H^+]} \text{ dm}^3 \text{ mol}^{-1} \qquad (2)$$

$$\bar{j} = \frac{[HB^+]}{[HB^+] + [B]} = \frac{\delta_{obs.} - \delta_0}{\delta_1 - \delta_0} \qquad (3)$$

mixtures, each containing the same total amount of Co (*i.e.* $[HB^+] + [B]$ = constant) together with increasing concentrations of perchloric acid, was prepared in D_2O, $Na[ClO_4]$ being added to maintain a constant ionic strength (0.33 mol dm^{-3}). All the shifts were measured with respect to 1,4-dioxan as internal standard. A value of K_1 was calculated using a least-squares computer program which outputs $\bar{j}(\log[H^+] - 0.4)$ and gave $K_1 = 3.06 \pm 0.18$ dm³ mol^{-1}.

Irradiation technique. All the irradiations were carried out on an optical bench equipped with a high-pressure mercury arc (Wotan HBO 200W) powered by a constant-current supply stabilised to 0.1%. The lamp output was collimated and passed through suitable Balzer-metal interference filters or a combination of glass filters and then the quartz photolysis cell. (The last two items were cooled by continuously flowing mains water.) The transmitted irradiation intensity was *ca.* 5×10^{-8} einstein s^{-1}.* The cell was cylindrical (5 cm long × 2 cm diameter) and was fitted with a greaseless Teflon tap enabling the circulation of argon to remove oxygen prior to irradiation, following which optical changes were determined by transferring the cell, suitably wrapped in a thick black cloth, to a Cary 14 spectrophotometer. Irradiation times were generally very short (10—10^2 s) and were measured with a stopwatch. The Balzer filters used transmitted light at 439, 408, 380, 363, and 313 nm (*ca.* ±20 nm). Also used was a Chance OV 1 filter, transmission 380 ± 40 nm, and a Bausch and Lomb monochromator (model no. 33-86-26-07). Solutions at

* 1 einstein = $N_A h\nu$ J mol^{-1}.

pH 2 and 7 were made up to absorbances of *ca.* 1.5—2 and 0.6 respectively at the irradiation wavelength.

Actinometry was performed using $K_3[Fe(C_2O_4)_3]$.[21] Quantum yields were evaluated with the aid of a computer program which included a correction for the increased level of transmitted light as reaction proceeded.[22]

RESULTS

Quantum Yields (all refer to Anaerobic Solution).—At pH 2, photolysis in the wavelength range 313—440 nm resulted in the gradual loss of absorption due to the alkylaquocobaloxime until virtually no absorption remained at $\lambda > 350$ nm.

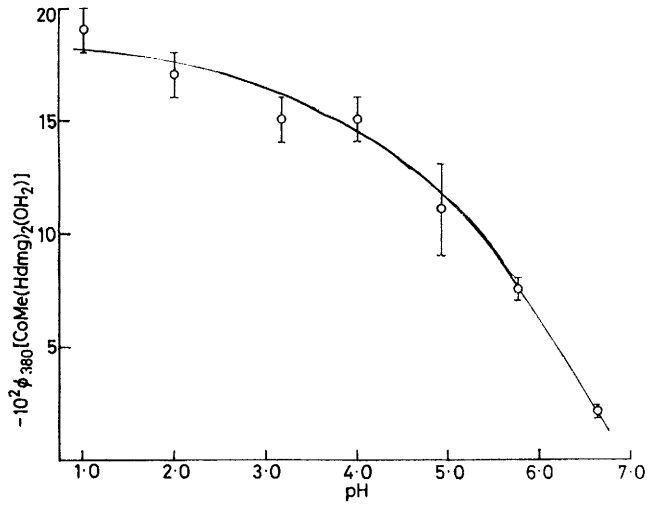


FIGURE 1 Acid dependence of the photodecomposition yield at 380 nm of aquomethylcobaloxime in deaerated dilute buffer solutions

The individual absorbances at various times at the irradiation wavelength of 380 nm fitted the classical photochemical decay kinetics and results for $\phi_{dec.}$ (380 nm) for a series of alkylaquocobaloximes are given in Table 3. $\phi_{dec.}$ for aquomethylcobaloxime was wavelength invariant at pH 2, lying in the range 0.14—0.17 for λ 313, 335, 363, 380, 408, and 439 nm. $\phi_{dec.}$ (380 nm) was strongly dependent on pH (Figure 1) and at pH 7 it was clear that, instead of simply

TABLE 3

Photodecomposition quantum yields of alkylaquocobaloximes [CoR(Hdmg)$_2$(OH$_2$)] at pH 2 (HCl–KCl) for irradiation at 380 nm

R	$\phi_{dec.}$
Me	0.17 ± 0.01
Et	0.27 ± 0.01
Pr^n	0.14 ± 0.005
Pr^i	0.24 ± 0.02
n-C_6H_{13}	0.12 ± 0.01

decomposing, all the alkylaquocobaloximes transformed to a new compound, $\lambda_{max.}$ 462 nm (Figure 2). This is identified as $[Co^{II}(Hdmg)_2(OH_2)_2]$ by comparison with authentic material (prepared after Schrauzer [19]) both spectrally and by virtue of its similar high reactivity towards acid and O_2.[23]

Gaseous hydrogen. This was detected unambiguously by g.l.c. from a solution of aquoethylcobaloxime at pH 7 following irradiation at $\lambda > 300$ nm. The instrument used was a Pye 104 chromatograph fitted with a katharometer detector using argon as carrier gas. Good separation from

TABLE 4

Hydrocarbon products from the photolysis of alkylaquocobaloximes [CoR(Hdmg)$_2$(OH$_2$)] in aqueous solution

R	pH 2	pH 7
Me	CH_4, C_2H_6	CH_4, C_2H_6
Et	C_2H_6, n-C_4H_{10}	C_2H_4
Pr^n	n-C_3H_8, $MeCH{=}CH_2$, n-C_6H_{14}	$MeCH{=}CH_2$
Pr^i	n-C_3H_8, $MeCH{=}CH_2$, $Me_2CHCHMe_2$	$MeCH{=}CH_2$
n-C_6H_{13}	n-$C_{12}H_{26}$ (0% C_6 products)	hex-1-ene
$PhCH_2$	bibenzyl (72%)	
$Ph(CH_2)_3$	$PhCH_2CH_2Me$ (50.5%) $PhCH_2CH{=}CH_2$ (25.8%) $Ph(CH_2)_6Ph$ (16.5%)	$PhCH_2CH{=}CH_2$

O_2 and N_2, introduced during injection, was achieved using a 2-m column of Linde 5A molecular sieves at 323 K.

Hydrocarbon products. These were investigated both at pH 2 and 7 and the results are summarised in Table 4. A

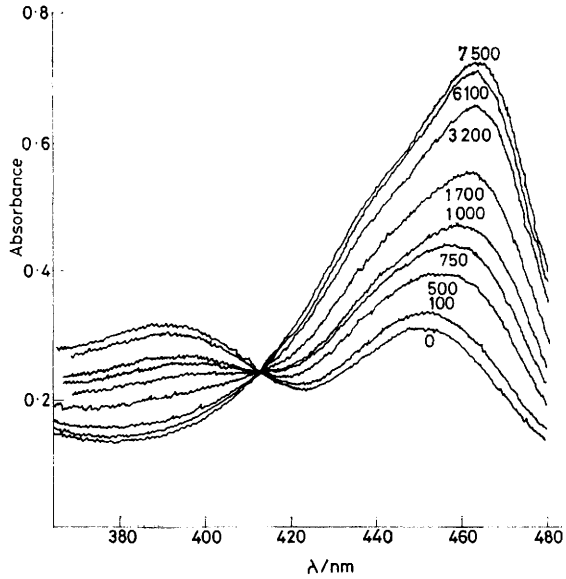


FIGURE 2 U.v.–visible profile of the 380-nm irradiation of aquo-n-propylcobaloxime in deaerated pure, neutral water. The numbers refer to *t*/s

clear dichotomy exists except in the atypical case of R = Me; the product at pH 7 is exclusively the alk-1-ene derived from R, whilst at pH 2 there is a preponderance of products derived by abstraction and dimerisation reactions of R$^{\bullet}$.

TABLE 5

Isotopic composition of methane and ethane in the photolysis of aquomethylcobaloxime in aqueous solution at pH 2

Cobaloxime	Solvent	Products
[CoMe(Hdmg)$_2$(OH$_2$)]	H_2O	CH_4, C_2H_6
[Co(CD$_3$)(Hdmg)$_2$(OH$_2$)]	H_2O	CD_3H, C_2D_6
[CoMe([$^2H_{12}$]Hdmg)$_2$(OH$_2$)]	H_2O	CH_4, C_2H_6
[CoMe(Hdmg)$_2$(OH$_2$)]	D_2O	CH_3D, C_2H_6

In order to identify the origin of the hydrogen appearing in the abstraction product, experiments were performed involving (*i*) CD_3(axial)-substituted methylcobaloxime, (*ii*) CD_3(Hdmg)-deuteriated methylcobaloxime, and (*iii*)

[21] C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc.*, 1956, **A235**, 518.

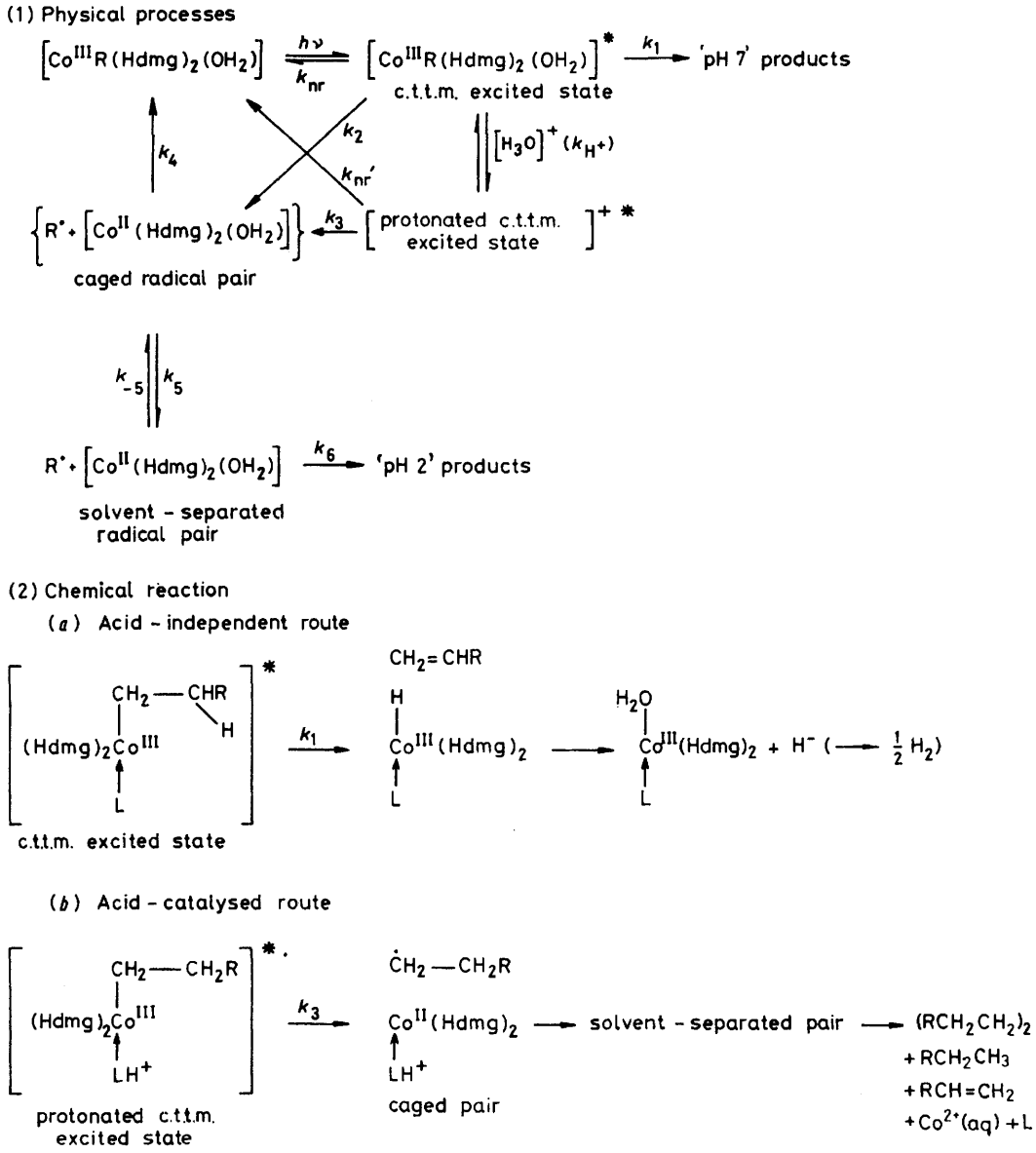
[22] T. J. Kemp and P. Moore, unpublished work.

[23] A. Adin and J. H. Espenson, *Inorg. Chem.*, 1972, **11**, 686.

D_2O as solvent, and the results are summarised in Table 5. The recovery of C_2D_6 from the CD_3 (axial)-substituted aquomethylcobaloxime at pH 2 is in essential agreement with the results of Schrauzer *et al.*[24] with axially deuteriated methylcobalamin and methyl(pyridine)cobaloxime at pH 7. Methyl radical does not abstract hydrogen from water,[25] and the failure of the photolysis of aquomethylcobaloxime fully deuteriated at the Hdmg methyl groups to produce CH_3D eliminates the latter groups as a possible hydrogen source. photolysis (as evinced by the induced radical transformation of added glycol,[4] the pattern of products from other alkylaquocobaloximes, *etc.*) indicates the former possibility as the more likely explanation.

DISCUSSION

Our essential finding is the absolutely crucial role of acidity in the aqueous solution photochemistry of alkyl-



SCHEME

The methane recovered always has one hydrogen atom bearing the same isotope as the aqueous solvent, which implies either attack of $CH_3^{\bullet}$ on the hydroxy group of the Hdmg (which exchanges rapidly with water) or neutralisation by solvent of a methyl anion produced in a primary photoheterolysis. The general free-radical character of the aquocobaloximes. (We had commenced work using other axial bases, especially pyridine, but under our reaction conditions base exchange occurred rapidly and we changed to aquocobaloximes to reduce the ensuing complications.) Not only do mild acidities (pH 3)

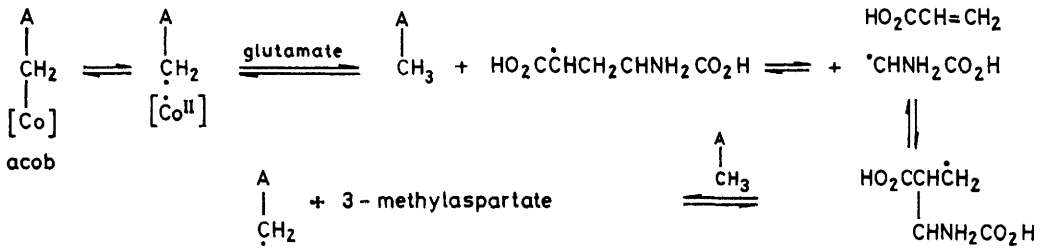
[24] G. N. Schrauzer, J. W. Sibert, and R. J. Windgassen, *J. Amer. Chem. Soc.*, 1968, **90**, 6681.

[25] B. C. Gilbert, R. O. C. Norman, G. Placucci, and R. C. Sealy, *J.C.S. Perkin II*, 1975, 885; J. K. Thomas, *J. Phys. Chem.*, 1967, **71**, 1919.

increase by ten-fold the rate of photodecomposition of cobaloximes over that prevailing at pH 7, but the course of reaction is changed both as regards the character of products afforded by the axial organic group (mostly RH + RR at pH 2, exclusively alkene at pH 7 except for R = Me) and the nature of the cobalt-containing product {aqueous cobalt(II) ion at pH 2, the complex $[Co^{II}(Hdmg)_2(OH_2)_2]$ at pH 7}. The ready acid decomposition of the latter might prompt consideration of it as an intermediate at all acidities, surviving only at neutral pH. That this possibility is an oversimplification is evident both from the strong catalysis of the photodecomposition and the characteristic products derived from R. The ground state of the cobaloxime is relatively unaffected by addition of acid: ^{1}H n.m.r. examination of the methyl protons at various acidities reveals a formation constant for $[CoR(H_2dmg)(Hdmg)(OH_2)]^+$ of 3.06 ± 0.18 dm^3 mol^{-1}, which is in good agreement with data obtained by other physical methods.[26] It is quite possible, however, that the excited state of the alkylcobaloxime is much more basic than the ground state, although in this case one might expect a sharper cut-off in the pH-profile of the quantum yield (Figure 1). An alternative possibility is that, while the excited state of the cobaloxime may not be subject to equilibrium protonation, its chemical breakdown may be acid-catalysed.

The dichotomy covers quantum yields, organic products, and cobalt(II) products, and suggests independent, parallel, acid-independent and acid-catalysed paths. The various possibilities can be presented as follows:

The independence of photodecomposition quantum yield over a wide wavelength range (which corresponds to excitation energies from 22 800 to 32 000 cm^{-1}) implies the presence of a stable charge-transfer-to-metal (c.t.t.m.) excited state rather than direct photodissociation into a radical pair.[27] This contrasts with the quite perceptible wavelength dependence of ϕ in the *aerobic* photolysis of various alkylcobalamins in aqueous solution;[17] also the pH-dependence is much less striking for the cobalamins. The breakdown (k_1) of the c.t.t.m. state for $[Co^{III}R(Hdmg)_2(OH_2)]$ (R $\neq$ Me) into alkene and a hydrido-complex (and thence gaseous hydrogen) is rather inefficient ($\phi \sim 0.02$), even so $k_1 \gg k_2$ because no radical-derived products are found at pH 7 in the absence of specific radical scavengers. (The non-radical character of the photolysis at pH 7 contrasts with the situation observed for non-aqueous media for which low-temperature e.s.r.[6] and spin-trapping studies[16] demonstrate radical intermediacy.) As indicated before, the acid-determined path to (initially) a caged radical pair can proceed either through equilibrium protonation of the c.t.t.m. state (which then decomposes with rate constant k_3) or through acid catalysis of k_2. The caged radical pair can then either collapse to regenerate starting material (k_4) or the components can diffuse apart (k_5), finally either recombining *via* homogeneous kinetics (k_{-5}) or forming products (k_6).



The production of alkene at pH 7 parallels the photochemical behaviour under visible light irradiation of $[Co(CHR^2CHR^1R)(Hdmg)_2(py)]$ in 1,4-dioxan solution, which produces $RCR^1{=}CHR^2$ and $[CoH(Hdmg)_2(py)]$ (the latter characterised by its reaction with phenylacetylene).[28] The presence of alkene at pH 2 in certain cases (Table 4) accords with the observed disproportionation–recombination ratios[29] of 0.15 (Et·), 0.14 (Pr^{n}·), and 1.2 : 1 (Pr^{i}·), although the rather high yield of alkene in the case of aquo(3-phenylpropyl)cobaloxime may result from competition by a particularly favoured elimination even at pH 2.

Aquo(3-phenylpropyl)cobaloxime was investigated in order to test a potential model system for the B_{12}-dependent enzyme glutamate mutase which interconverts (*S*)-glutamate and (2*S*,3*S*)-3-methylaspartate.[30] A hypothetical mechanism for this enzymatic reaction involving radical intermediates is shown above (*cf.* ref. 30). It was therefore of interest to examine the photodecomposition of aquo(3-phenylpropyl)cobaloxime since this substance might reveal an analogous fragmentation to that proposed, giving ethylene and the benzyl radical. The latter could give rise to bibenzyl and toluene. However, neither at pH 2 nor 7 was any trace of these products observed.

In conclusion we note that acidic pH influences the photochemistry of systems containing alkylcobaloximes in *three* ways relevant to their use as models for B_{12}-dependent processes: (*i*) the rate of photochemical breakdown of the cobaloxime is accelerated; (*ii*) free

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radicals are produced from the alkyl group, whereas at pH 7 only a radical pair may arise; and (*iii*) the transformation of a glycol radical to an aldehyde radical is acid-catalysed.[4]

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