Nonenzymic Model of the Dioldehydratase Reaction. Initiation of Conversion of Ethylene Glycol into Acetaldehyde on Anaerobic Photolysis of Organocobalamins in the Presence of SH-Compounds

By INNA P. RUDAKOVA, T. E. ERSHOVA, A. B. BELIKOV, and A. M. YURKEVICH
(*The All-Union Scientific Vitamin Research Institute, Nauchny pr.* 14A, *Moscow* 117246, *U.S.S.R.*)

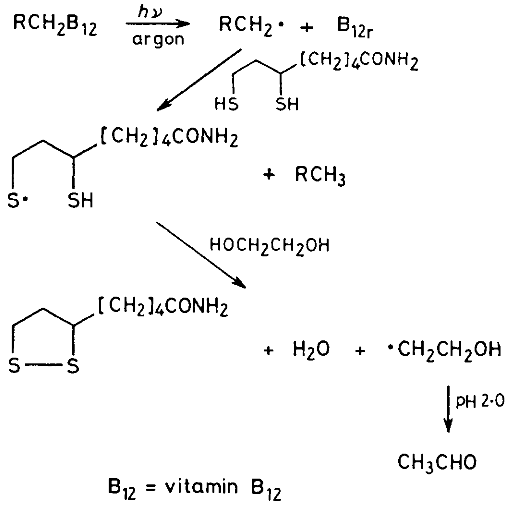
Summary Anaerobic photolysis of adenosyl- and methylcobalamins in an aqueous KCl–HCl buffer (pH 2·0) in the presence of SH-compounds (*e.g.* dihydrolipoic acid amide) causes conversion of ethylene glycol into acetaldehyde, and provides a model for the dioldehydratase enzymic reaction.

ONE of the enzymic reactions catalysed by the vitamin B$_{12}$-dependent enzymes is the conversion of 1,2-diols into the correspondent aldehydes. It was found that Co(α)-[α-(5,6-dimethylbenzimidazolyl)]-Co(β)-adenosylcobamide (adenosylcobalamin, AdoCbl) has a similar function to that of dioldehydratase coenzyme.[1] The mechanism of these biochemical reactions is currently under extensive study. The e.s.r. spectra observed during the dioldehydratase enzymic reaction provide evidence for a homolytic mechanism for cleavage of the coenzyme Co–C bond and the formation of vitamin B$_{12r}$ and organic radicals during the enzymic catalysis.[2] Homolytic cleavage of the Co–C bond in organocobalamins can be initiated photochemically or thermally. It has been shown that the photochemical process involves homolytic cleavage of the Co–C bond with formation of vitamin B$_{12r}$ and organic radicals.[3]

Recently Golding *et al.*[4] described the nonenzymic conversion of ethylene glycol into acetaldehyde initiated by photolysis of methyl(aquo)cobaloxime in an aqueous buffer (pH 2·0) by irradiation with monochromatic light of wavelength 380 ± 15 nm. A pH of 2·0 was chosen on the basis of an investigation[5,6] of the influence of protonation of hydroxyethyl and other radicals on the 1,2-shift, in which it was found that protonation considerably reduces the activation energy (by up to 8·3 kcal/mol) owing to inductive electron withdrawal from the radical centre. The acetaldehyde formed under these conditions was isolated as its 2,4-dinitrophenylhydrazone (DNP) derivative. The concentration of methyl(aquo)cobaloxime was 250 times less than that of ethylene glycol and it was assumed[4] that the acetaldehyde was formed non-enzymically from ethylene glycol with the participation of methyl radicals produced from photolysis of the methyl(aquo)cobaloxime. However, use of methyl(aquo)cobaloxime as the methyl radical donor upon photolysis may be complicated in view of the recent discovery of photochemical reactions involving electronic transfer from the equatorial ligands to the central cobalt atom with the formation of a Co^{II}-compound containing both the axial ligands.[7]

We have already shown[8] that on photolysis of AdoCbl in the presence of SH compounds in 0·05 M potassium phosphate buffer (pH 7·4) 5′-deoxyadenosine is formed. In a search for nonenzymic model reactions catalysed by AdoCbl we have studied the transformations of ethylene glycol initiated on photolysis of AdoCbl under various conditions. Photolysis was performed with a 100 W tungsten lamp in aqueous KCl–HCl buffer (pH 2·0) both in the presence and the absence of dihydrolipoic acid amide, for solutions (15 ml) containing 0·065 g (0·04 mmol) of AdoCbl, 0·10 g (0·4 mmol) of dihydrolipoic acid amide and 5 ml of a 5M aqueous solution of ethylene glycol (1·55 g) (25 mmol). Two control experiments were carried out: irradiation of ethylene glycol in aqueous KCl–HCl buffer under argon and irradiation of ethylene glycol in the same buffer in the presence of dihydrolipoic acid amide. The composition of the solutions after irradiation showed that at pH 2·0 as well as in neutral medium anaerobic photolysis of AdoCbl leads to the formation of 8,5′-cycloadenosine and in the presence of dihydrolipoic acid amide 5′-deoxyadenosine is formed, as shown before.[8] The aldehydes formed during the photolysis were isolated as their DNPs by t.l.c. on Woelm and Silufol Kavalier. The DNPs were analysed quantitatively by t.l.c. on Silufol in chloroform and in ethyl acetate–hexane (3 : 7). Acetaldehyde was not formed on photolysis of ethylene glycol in the presence of AdoCbl but in the absence of SH compounds, but it was formed in the presence of AdoCbl and dihydrolipoic acid amide. The acetaldehyde DNP isolated was identified by comparison (m.s., u.v., n.m.r., and t.l.c.) with authentic material. The yield of acetaldehyde DNP was *ca.* 30% (u.v. spectroscopy) based on AdoCbl or MeCbl.

We have also studied the transformations of ethylene glycol induced by the photolysis of Co(α)-[α-(5,6-dimethylbenzimidazolyl)]-Co(β)-methylcobamide (MeCbl) under the same conditions as for AdoCbl. On photolysis in the absence of dihydrolipoic acid amide acetaldehyde was not observed, as with AdoCbl, whereas the presence of SH-compounds led to conversion of ethylene glycol into acetaldehyde. We have also observed the formation of acetaldehyde in the reaction solution (pH 7·4) in the presence of SH compounds. A possible mechanism for this conversion is shown in the Scheme.



SCHEME

(*Received*, 3*rd November* 1977; *Com.* 1144.)

---

[1] T. C. Stadtman, *Science*, 1971, **171**, 859.

[2] T. H. Finlay, J. Valinsky, A. S. Mildvan, and R. H. Abeles, *J. Biol. Chem.*, 1973, **248**, 1285.

[3] J. Halpern, *Ann. New York Acad. Sci.*, 1974, **239**, 2.

[4] B. T. Golding, T. J. Kemp, E. Nocchi, and W. P. Watson, *Angew. Chem.*, 1975, **87**, 841.

[5] B. T. Golding and L. Radom, *J.C.S. Chem. Comm.*, 1973, 939.

[6] B. T. Golding and L. Radom, *J. Amer. Chem. Soc.*, 1976, **98**, 6331.

[7] C. Giannotti and J. R. Bolton, *J. Organometallic Chem.*, 1976, **110**, 383.

[8] I. P. Rudakova, E. G. Chauser, and A. M. Yurkevich, *Bio-organic Chem.*, 1975, **1**, 616.

[9] M. E. Mason, B. Johnson, and M. C. Hamming, *Analyt. Chem.*, 1965, **37**, 761.

[10] J. Seibl, *Helv. Chim. Acta*, 1967, **50**, 263.