The results reflect the complexity of each system, the simultaneous presence of several species in them, the sensitivity of the complex formation equilibria on internal (structure of ligand) and external (matrix) factors. The equilibrium constants have been used for the calculation of the concentration distribution of species of different compositions.

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B6

A New Model of Coenzyme B_{12}?

I. YA. LEVITIN* and M. E. VOL'PIN

Institute of Organo-Element Compounds, Academy of Sciences of the U.S.S.R., Moscow B-334, U.S.S.R.

A survey of vitamin B_{12}-dependent rearrangements suggests that they involve homolytic splitting of the Co–C bond in 5′-deoxyadenosylcobalamin. Numerous attempts were made to simulate these processes using 5′-deoxyadenosylcobalamin in nonenzymatic systems as well as its most popular models, organocobaloximes. Nevertheless, striking features of the homolysis step, namely mild conditions, reversibility and controllability, have been neither imitated nor properly explained so far. In this connection, certain results of our studies with a new type of organocobalt chelate [1] may be of interest.

The cationic complexes in question involve the trivalent metal bound to an alkyl group, a chelating diamine and a mixed tridentate ligand derived from a Schiff base constituted by the same diamine and an *o*-hydroxycarbonyl compound at a 1:1 ratio. Conditions of their formation and its mechanism are considered; the spatial and electronic structure of the complexes is also studied. Some of the reactions related to modelling vitamin B_{12} (*e.g.* photolysis, reduction and oxidation) are discussed, with emphasis being put on the unusual behaviour of the complexes under the influence of acids [2].

Decomposing readily in acidic media, the alkylcobalt chelates under consideration give all the products of disproportionation and coupling of the alkyl groups (RH, R_{-H} and R_2), the yields of the RH alkanes being substantially higher than those of alkenes. Experiments with an isotope label (D_2O) revealed that the excess of the former was due to the abstraction of hydrogen atoms from chelating ligands by alkyl free radicals rather than to protolysis of the Co–C bond. These findings suggest homolytic cleavage of the organocobalt complexes under the action of protons.

The formation of alkyl free radicals in the course of decomposition was directly proved by the spin-trapping technique. Spin adducts of the radicals (*viz.* Me, Et and *c*-C_6H_{11}) with Bu^tNO and $PhCH{=}N(O)Bu^t$ were identified by ESR spectroscopy in phosphate buffer solutions. Furthermore, kinetic measurements with the latter trap at various pHs indicated that protons are involved in steps leading to the formation of alkyl free radicals. The intermediacy of protonated complexes still holding the Co–C bond was established by means of spin-trapping, NMR and spectrophotometric techniques.

The ability of the complexes in question to generate alkyl free radicals under mild conditions and at a conveniently regulated (pH-controlled) rate was used to imitate vitamin B_{12}-dependent dehydration of α-glycols. Some positive results give support to the speculation that protonation-deprotonation or related polar interactions may control the dissociation of the Co–C bond of 5′-deoxycobalamin in enzymatic systems, thus triggering the biological dehydratation of glycols as well as other vitamin B_{12}-dependent rearrangements.

The potential use of the complexes as sources of free radicals in living organisms is also discussed.

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B7

Iron–Carbon Bond Formation During Substrate Activation by Hemoproteins

D. MANSUY

Laboratoire de Chimie de l'Ecole Normale Supérieure, 24, rue Lhomond, 75231 Paris Cédex 05, France

Recent results point to the existence of an important organometallic chemistry of certain hemoproteins, with the formation of iron–carbon bonds during substrate activation. Evidence for such iron–carbon bond formation comes both from spectroscopic studies on the hemoproteins themselves and from model studies on iron-porphyrins. These iron–carbon bonds are formed either upon reduction or oxidation of several substrates [1].

Reduction of benzylhalides, $ArCH_2X$, by microsomal cytochrome P450 leads to σ-alkyl complexes of this cytochrome involving a $Fe(III)–CH_2Ar$ bond. Reduction of halothane, $CF_3CHClBr$, leads also to a σ-alkyl cytochrome $P450–Fe(III)–CHClCF_3$