EPR Characterization of the Photolysis and Thermolysis Products of Alkylcobaloximes with Symmetric Phosphines and Phosphites. Factors That Stabilize the Cobalt Homolysis Fragments

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The products of anaerobic photolysis of several alkylcobaloximes with symmetric phosphines and phosphites were studied by electron paramagnetic resonance spectroscopy in nonaqueous solutions and at several temperatures. Evidence is provided for photochemically induced homolytic cleavage of the cobalt–carbon bond and for the formation of stable cobalt(II) five-coordinated species and of organic radicals as homolysis products. The resulting cobalt(II) species are independent of the alkyl group of the cobaloxime, as the EPR spectra of the different alkylcobaloximes with the same phosphorus ligand are identical. A rationale for the lack of reactivity of the cobalt(II) five-coordinated species is provided by an analysis of the EPR parameters and the use of extended Hückel calculations that show the cobalt atom to lie well above the equatorial coordination plane defined by the glyoximes, thus rendering the sixth position not easily available for coordination.

Introduction

The recognition that homolysis of the Co–C bond in coenzyme B_{12} (5′-deoxyadenosylcobalamin) dependent rearrangements is the only role identified thus far for this cofactor has spurred a new interest in the aspects that promote cleavage of this bond.[1-3] Conformational changes in both coenzyme B_{12} and the protein upon addition of the substrate to the holoenzyme have been widely accepted to be responsible for enzyme-accelerated Co–C bond cleavage. An enzyme-induced distortion of the corrin ring toward the adenosyl moiety reminiscent of the butterfly conformation observed in the corrin,[2-5] a lengthening of

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