The Methylation of the Mercuric Ion by Methylcobaloximes

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Cobaloximes and certain other cobalt complexes have recently been of interest as model compounds of vitamin B_{12}, and the chemistry involving the Co–C bond has been extensively investigated, particularly in connection with cobaloximes.[1]

It has been reported that Hg^{2+} is alkylated by alkylcobalamin, in the presence of a reducing agent, both enzymatically and nonenzymatically, to produce monoalkyl and dialkyl mercury.[2] Recently, Ukita *et al.*[3] found that the methylation of Hg^{2+} to afford monomethyl and/or dimethyl mercury took place by means of methylcobalamin in the absence of a reducing system. In view of the stability of the alkyl-cobalt bond,[4,5] the facile cleavage of the bond by Hg^{2+} to form alkyl mercurials is worthy of note.

Prompted also by the previous report that methylpentacyanocobalt complex can transfer its methyl group to Hg^{2+},[6] we were led to simulate the nonenzymatic reaction with methylcobaloximes and $HgCl_2$ in the absence of reducing agent and in a phosphate buffer solution. As a result, we found that the expected methylation took place although only methylmercuric chloride was formed.[7] The transmethylation may be represented by

$$CH_3\text{–(Co)–B} + HgCl_2 \xrightarrow[pH=7.0]{37^\circ, \text{dark}} CH_3HgCl + HO\text{–(Co)–B} + Cl^-$$

where (Co)-B denotes the cobaloxime moiety, with B representing an axial base such as H_2O or imidazole. Figure 1 shows the yield of the product with the time.

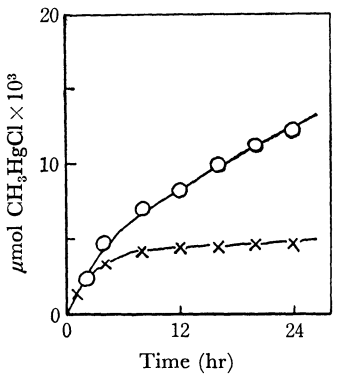

Fig. 1. The time course for the formation of CH_3HgCl in the dark at 37°C under an aerobic condition.
The reaction contained 0.1 μmol methylcobaloxime and 0.05 μmol $HgCl_2$ in 0.25M phosphate buffer at pH 7.0.
—○— methyl(imidazole)cobaloxime
—×— methyl(aquo)cobaloxime

It is apparent from Fig. 1 that the imidazole-coordinated cobaloxime is more reactive than the aquo-complex. This phenomenon is in accord with the kinetic data on the similar reaction between methylcobalamin or methylcobinamide and Hg^{2+}.[8] Also, it is to be noted that the methylcobaloxime is less reactive than the methylcobalamin, as is demonstrated by the formation of dimethyl mercury with the cobalamin. The difference in reactivity between the cobaloxime and the cobalamin is consistent with their electronic nature.[9] It is obvious, however, that the methylcobaloximes are reactive enough to methylate Hg^{2+} to yield monomethyl mercury.

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