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De-alkylation Reactions of Alkylcobaloxime Complexes with Mercury(II)†

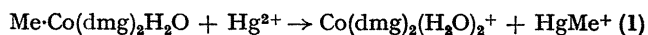
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Summary The kinetics of the reactions of a series of alkylcobaloxime complexes with the mercury(II) ion, in which alkylmercury(II) ions are formed, suggests a bimolecular mechanism of electrophilic substitution.

EARLY examples of aliphatic electrophilic substitution reactions involved the transfer of alkyl groups between two mercury complexes.¹ The reactions of $\text{Hg}(\text{OAc})_2$ with alkyl cobalt(III) corrinoids,² and of Hg^{II} and its complexes with pyridiomethyl derivatives of $(\text{H}_2\text{O})_5\text{Cr}^{\text{III}}$ and $(\text{NC})_5\text{Co}^{\text{III}}$ have since been studied.³

Various alkyl cobaloxime‡ complexes, $\text{R}\cdot\text{Co}(\text{dmg})_2\text{B}$, [(dmg) = dimethylglyoxime], have chemical reactions similar to those of corresponding corrinoids. We report that the alkylaquocobaloxime complexes undergo de-alkylation upon reaction with mercury(II), as illustrated by the methyloquo-complex in equation (1).



The monomethylmercuric ion was identified by precipitation of the bromide and iodide salts whose m.p.s and i.r. spectra corresponded to those of an authentic sample. The Co^{III} product was verified spectrophotometrically, and also by its adsorption into Dowex 50W-X8 cation exchange resin, from which it could be removed by 0.2M- HClO_4 . Spectrophotometric titrations confirmed the 1:1 stoichiometry, which was also supported by the 76% isolated yield of MeHgBr from a 0.01M reaction solution. In other cases the alkylmercuric chloride salt was precipitated after the reaction and identified by its m.p. The only exception to this stoichiometry is found for $\text{R} = \text{CH}_2\text{Cl}$, where Hg_2Cl_2 is isolated. It was shown, however, that under these conditions HgCH_2Cl^+ is decomposed to Hg_2^{2+} by excess of Hg^{2+} .

The reaction kinetics were followed spectrophotometrically; the absorption band characteristic of the alkyl complexes ($\lambda_{\text{max}} \sim 450 \text{ nm}$, $\epsilon \sim 1.5 \times 10^3$) virtually disappears ($\epsilon_{\text{prod}} \sim 2 \times 10^2$) upon reaction with Hg^{2+} . The rates were evaluated in the presence of excess of Hg^{2+} and obey a simple second-order rate law [equation (2)].

$$d[\text{HgR}^+]/dt = k_2[\text{R}\cdot\text{Co}(\text{dmg})_2\text{H}_2\text{O}][\text{Hg}^{2+}] \quad (2)$$

The rate decreases markedly with increasing $[\text{H}^+]$; a plot of k_2^{-1} vs. $[\text{H}^+]$ was linear (Figure), consistent with equa-

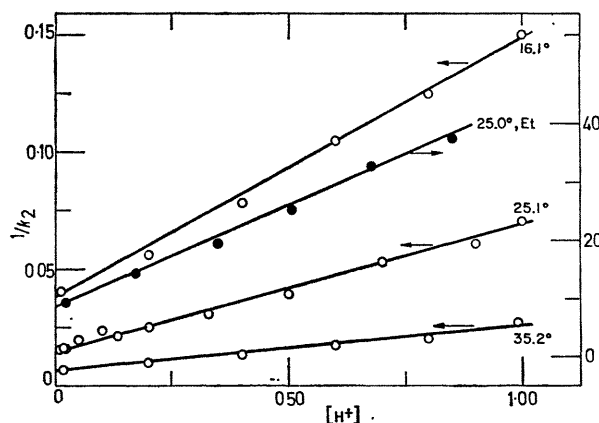


FIGURE. Representative plots of the reciprocal of the apparent second-order rate constant vs. $[\text{H}^+]$ for $\text{R} = \text{Me}$ (\circ , left ordinate) and $\text{R} = \text{Et}$ (\bullet , right ordinate).

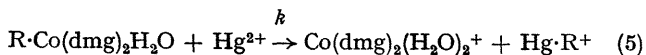
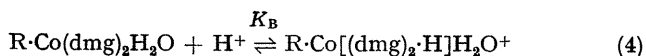
tion (3). The following mechanism, equations (4) and (5),

$$k_2 = A/\{1 + B[\text{H}^+]\} \quad (3)$$

is in agreement with the kinetic data with A and B identified,

† Work performed in the Ames Laboratory of the U.S. Atomic Energy Commission.

‡ A trivial name for the compounds alkylaquobis(dimethylglyoximato)cobalt(III).



respectively, as k and K_B . Like other cobaloximes, the alkyl complexes behave as weak bases [equation (4)]. The spectrum of the cobaloxime was sensitive to $[\text{H}^+]$; the change in absorbance with $[\text{H}^+]$ was small, but did afford an independent determination of K_B . The rate and

spectral changes with $[\text{H}^+]$ as $\text{Me}\cdot\text{Co}(\text{dmg})_2\text{H}_2\text{O}$ does, and because the spectrum of the BF_2 derivative⁴ [structure (II)], which cannot undergo protonation as shown in (I), is relatively insensitive to large changes in $[\text{H}^+]$. The i.r. studies⁶ indicate a structure analogous to (I) for the "dichloro-acid", $\text{HCo}(\text{dmg})_2\text{Cl}_2$; we have isolated a solid having the approximate composition $\text{Me}\cdot\text{H}\cdot\text{Co}(\text{dmg})_2\text{SCN}$.

The second-order kinetics indicate that electrophilic substitution proceeds by an S_E2 or S_Ei mechanism.¹ The reaction rate of the methyloquo-complex was drastically

TABLE. Kinetic and equilibrium parameters for $\text{R}\cdot\text{Co}(\text{dmg})_2\text{H}_2\text{O}-\text{Hg}^{2+}$ reactions^a

R	K_B / M^{-1}			$\Delta H^\ddagger / \text{kcal mol}^{-1}$	$\Delta S^\ddagger / \text{cal mol}^{-1} \text{deg}^{-1}$
	kinetic	spectro-photometric ^b	$k / \text{M}^{-1} \text{s}^{-1}$		
Me	3.5 ± 0.2	3.23 ± 0.15	65 ± 2	16.2	4
Et	4.2 ± 0.4	3.4 ± 0.2	0.121 ± 0.007	20.5	6
Pr ^a	4.3 ± 0.1	—	0.092 ± 0.003	20.3	5
Pr ^t	—	4.2 ± 0.3	$< 7 \times 10^{-6c}$	—	—
Bu ^t	4.1 ± 0.1	—	0.36 ± 0.02	19.9	6
CH_2Cl^d	—	1.00 ± 0.08	2.6×10^{-4}	—	—
Me, BF_2 derivative (II)	—	v. small	$< 3.5 \times 10^{-4e}$	—	—

^a Aqueous solutions at 25° and 1.0M ionic strength maintained by perchloric acid-lithium perchlorate. The uncertainties indicate one standard deviation.

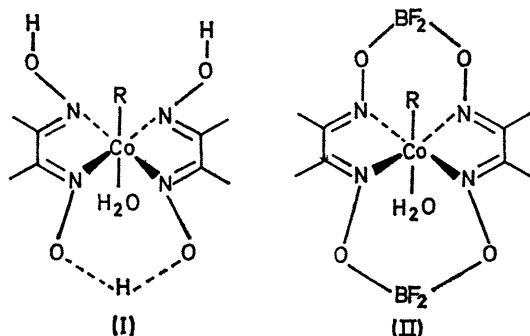
^b Ca. 21°. Values of K_B are rather insensitive to temperature.

^c Considerable quantities of Hg_2^{2+} were formed.

^d Because of a very stable pre-association with Hg^{2+} , this value represents the value of k for the reaction of $\text{HgClCH}_2\cdot\text{Co}(\text{dmg})_2\text{H}_2\text{O}^{2+}$ with Hg^{2+} .

^e Only an upper limit is cited because the spontaneous decomposition is appreciable.

equilibrium constants are summarized in the Table, along with the activation parameters computed from the temperature dependence of the bimolecular rate constant k for reaction (5). No kinetic or spectrophotometric evidence was found for appreciable complexation or association of Hg^{2+} and the cobaloxime, except in the case $\text{R} = \text{CH}_2\text{Cl}$ where a very strong adduct is formed ($K \geq 5 \times 10^6 \text{M}^{-1}$), which was decomposed by a second Hg^{2+} .



The protonation equilibrium is attributed to a protonation of one end of the planar, hydrogen-bonded dimethylglyoxime framework, as in structure (I), because solutions of the complex⁵ $[\text{Me}\cdot\text{Co}(\text{dmg})_2\text{SCN}]^-$ undergo the same

reduced by addition of Cl^- , whereas a faster reaction of HgCl^+ would have been expected had the reaction proceeded by a cyclic transition state involving mutual substitution at Hg and Co (S_Ei mechanism).

The effects of substituents at the α and β carbon atoms of R also support an S_E2 mechanism. The former is accompanied by marked rate effects ($\text{Me} > \text{Et} > \text{Pr}^t$), whereas the latter is nearly without effect ($\text{Et} \sim \text{Pr}^a \sim \text{Bu}^t$). This is consistent^{1,7} with the attack of Hg^{2+} on the same side of the α carbon as the Co atom. A substantial rate effect was also noted for α carbon substitution for the electrophilic attack of $\text{Hg}(\text{OAc})_2$ on alkyl cobalt corrinoids.⁸ Similar 'adjacent' attacks have been demonstrated by the retention of configuration of the α carbon in mercury-for-mercury substitutions,^{1,7} and in the electrophilic cleavage of alkyl groups from $\text{R}\cdot\text{Mn}(\text{CO})_5$ by bromine.⁸

The low reactivity of the BF_2 derivative (II) may arise from steric crowding of the proposed configuration-retaining transition state, as may the negligible reactivity of the protonated species. However, both compounds are also subject to an electronic inductive effect. The lower reactivity of the protonated species toward aquation was also noted; the relative rates of thiocyanate aquation of $[\text{Me}\cdot\text{Co}(\text{dmg})_2\text{SCN}]^-$ are 1:4.7 in 4*F* solutions of HClO_4 and LiClO_4 .

Further work on these and related systems is in progress.

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