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DEALKYLATION OF ALKYLCOBALT COMPLEXES BY THE MERCURY(II) ELECTROPHILE

VIRGIL E. MAGNUSON and JAMES H. WEBER

Department of Chemistry, Parsons Hall, University of New Hampshire, Durham, N.H. 03824 (U.S.A.)

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Summary

The dealkylation of a variety of $RCo(BDMBg)^+$ complexes by Hg^{2+} is discussed. (The ligand $BDMBg^-$ is formed by the condensation of two moles of 2,3-butanedionemonoxime with one mole of 1,3-propanediamine or 1,2-ethanediamine.) The products of the dealkylation reaction are $Co^{III}(BDMBg)(H_2O)_2^{2+}$ and RHg^+. All reactions are first order in the $[Hg^{2+}]$. The second order rate constants (k_2) vary from 5.9 M^{-1} sec^{-1} ($R = CH_3$) to 5.7×10^{-3} M^{-1} sec^{-1} ($R = n\text{-}C_3H_7$). The relative rates for R are: $CH_3 \gg C_2H_5 > C_6H_5CH_2 > n\text{-}C_4H_9 \simeq n\text{-}C_3H_7$. This order and other evidence are indicative of an S_E2 mechanism with an attack by Hg^{2+} on the carbon bonded to the cobalt.

Introduction

In recent years there has been much interest in the reactions of alkylbis(dimethylglyoximato)cobalt(III) complexes, $RCo(DMG)_2(H_2O)$, and other alkylcobalt compounds [1, 2]. Of particular interest to this work are their reactions with mercury(II). The initial studies on the DMG system were done by Schrauzer et al. [3] in an aqueous acetic acid—sodium acetate buffer system, and later studies were done in aqueous perchloric acid systems [4, 5]. In addition the reactions of alkylcobalamins with Hg^{II} were studied [3, 6, 7].

The reactions between mercury(II) and $RCo(DMG)_2(H_2O)$ have a 1/1 stoichiometry and result in the products shown in eqn. 1. The alkylation is thought to occur by an S_E2 mechanism. In addition the reaction rate is known to have an

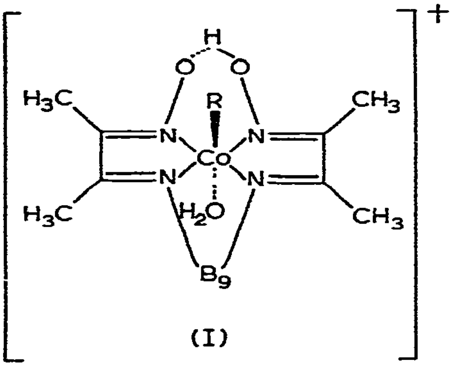
$$RCo(DMG)_2(H_2O) + Hg^{2+} \xrightarrow{H_2O} Co(DMG)_2(H_2O)_2^+ + RHg^+ \qquad (1)$$

inverse dependence on the $[H^+]$ [4, 5] due to the protonation of one hydrogen-bonded oxygen (eqn. 2). The equilibrium constant values, K_B, in aqueous $HClO_4$

$$RCo(DMG)_2(H_2O) + H^+ \overset{K_B}{\rightleftharpoons} RCo(DMG)(DMGH)(H_2O)^+ \qquad (2)$$

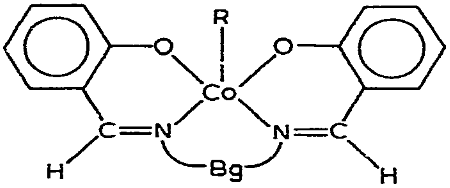
range from 1 to 5 M^{-1} depending on the R group. Alkyl groups have higher K_B values than aryl groups. Recently the protonated complex $[C_2H_5Co(DMG)(DMGH\,Cl] \cdot H_2O$ was isolated and its X-ray structure determined [8].

In this paper we will report on the dealkylation reactions of the complexes $[RCo(BDMBg)(H_2O)]^+$ (I) by mercury(II). (BDM = 2,3-butanedionemonoxime, Bg = bridging group). This work is part of a broad, systematic study of the reactions of cobalt—alkyl bonds in the BDMBg and sal_2Bg (II) systems. The nucleophilic attack of HS^- *trans* to the alkyl group in $RCo(sal_2Bg)$ has already been reported (sal = salicylaldehyde) [9].



(I)

$R = CH_3, C_2H_5, n\text{-}C_3H_7, n\text{-}C_4H_9, CH_2C_6H_5$
$Bg = (CH_2)_3, (CH_2)_2$



(II)

$R = CH_3, C_2H_5, n\text{-}C_3H_7$
$Bg = (CH_2)_2, CH_2CH(CH_3), CH_2C(CH_3)_2$

Results and discussion

The products of the reactions shown in eqn. 3 were identified; the cobalt complex by spectrophotometric comparison to an authentic sample, and the RHg^+ ($R = CH_3$) by the melting point of CH_3HgCl. The cobalt(III) product of the

$$RCo[BDM(CH_2)_3](H_2O)^+ + Hg^{2+} \rightarrow Co^{III}[BDM(CH_2)_3](H_2O)_2^{2+} + RHg^+ \qquad (3)$$

reaction is analogous to that found in the DMG system (eqn. 1) and the monoalkylmercury cations are identical. An attempt to determine the stoichiometry of reaction 3 failed due to its slow rate, but it is probably the 1/1 stoichiometry found in the DMG system (eqn. 1).

The kinetic behavior of the reaction of $RCo[BDM(CH_2)_3](H_2O)^+$ with Hg^{2+} is similar to that of the analogous DMG complexes under pseudo-first-order conditions. With an excess of Hg^{2+} rate law 4 is observed. Pseudo-first-order

$$-d[RCo]/dT = k_{obs}[RCo] \qquad (4)$$

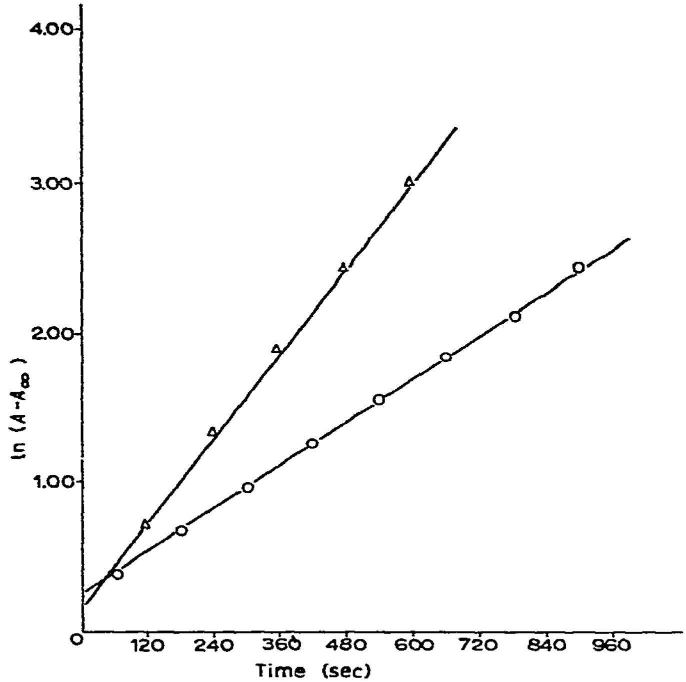


Fig. 1. Representative plots of ln $(A-A_\infty)$ vs. time at 25°C and $[Hg^{2+}]$ 0.4 M. ○, n-$C_3H_7Co[BDM(CH_2)_3]$-$(H_2O)^+$; △, $C_2H_5Co[BDM(CH_2)_3](H_2O)^+$.

rate plots (Fig. 1), which were always linear over at least three half-lives, yielded values of k_{obs} from the slopes. The $[Hg^{2+}]$ dependence of the reactions was determined by varying the $[Hg^{2+}]$ from 0.01 to 0.4 M while keeping the ionic strength at 2.2 and the $RCo[BDM(CH_2)_3](H_2O)^+$ concentration near 4×10^{-4} M. Because the first order $[Hg^{2+}]$ dependence is proven by the straight lines of the typical k_{obs} vs. $[Hg^{2+}]$ plots shown in Fig. 2, the rate law shown in eqn. 5 is correct. The k_2 values for the $Hg(ClO_4)_2$ system shown in Table 1 were obtained

$$-d[RCo]/dT = k_2\,[RCo]\,[Hg^{2+}] \qquad \text{where } k_2\,[RCo] = k_{obs} \tag{5}$$

from the slopes of similar graphs. A major difference between the $BDM(CH_2)_3$ and DMG complexes is that the reaction rates of $RCo[BDM(CH_2)_3](H_2O)^+$ are not dependent on the $[HClO_4]$ in the range 0.3 to 1.0 M. The hydrogen bonded oxygen in $RCo[BDM(CH_2)_3](H_2O)^+$ is a poorer base than the one in $RCo(DMG)_2$-(H_2O), predominantly because of the cationic nature of $RCo[BDM(CH_2)_3](H_2O)^+$. Except for the charge on the $BDM(CH_2)_3$ complex, the analogous alkyl DMG complexes are quite similar in many properties [10].

Our data for the complexes listed in Table 1 show the same trends shown by $RCo(DMG)_2(H_2O)$ [3, 4, 5] and by alkyl cobalamins [3]. The relative k_2 values are: $CH_3 \gg C_2H_5 > n\text{-}C_3H_7$ in all three systems. The trend is consistent with a bimolecular electrophilic substitution (S_E2) mechanism. If a *trans* attack occurred, the reaction order would be reversed as found for an alkyl—cobalt system containing tetradentate diimine ligands (II) [9]. The substitution of BF_2 for the hydrogen bonded proton forms $CH_3Co[BDM(CH_2)_3BF_2]^+$ which reacts 40000

TABLE 1

KINETIC DATA FOR THE REACTIONS OF $RCo[BDM(CH_2)_3](H_2O)^+$ WITH $Hg(ClO_4)_2$ [a]

R	k_2 (M^{-1} sec^{-1})
CH_3	5.9
C_2H_5	1.8×10^{-2} [b]
n-C_3H_7	5.7×10^{-3}
n-C_4H_9	6.1×10^{-3}
$CH_2C_6H_5$	7.7×10^{-3}
$CH_3(BF_2)$ [c]	1.5×10^{-4}
$C_2H_5[BDM(CH_2)_2]$ [d]	1.4×10^{-3}

[a] At 25°C with 1 M $HClO_4$ and μ maintained at 2.2 with $NaClO_4$ [b] Under the same conditions we observed for $C_2H_5Co(DMG)_2(H_2O)$ a k_2 value of 1.7×10^{-1} M^{-1} sec^{-1} and a K_B value of 4.9. The ref. 5 values are 1.2×10^{-1} M^{-1} sec^{-1} for k_2 and 3.9 for K_B. [c] BF_2 replaces the hydrogen bonded proton (see struc. I). [d] The bridge is $(CH_2)_2$ instead of $(CH_2)_3$ (see struc. I).

times slower than the hydrogen bonded analog. This result is in agreement with a bimolecular electrophilic attack because the electron-withdrawing effect of BF_2 makes the carbon less susceptible to an electrophilic attack.

The replacement of a $(CH_2)_3$ bridging group with a $(CH_2)_2$ also decreases the reaction rate of the C_2H_5 complex, but only by a factor of 13. This result can be explained by a steric effect. The shorter $(CH_2)_2$ bridge forces the oxime oxygens apart, and a weak hydrogen bond is formed if one occurs at all. The *cis* oxime nitrogens can twist out of the N_4Co plane and interfere with the Hg^{2+} attack. The non-planarity is also evidenced by the difficulty in synthesizing the $RCo[BDM(CH_2)_2]$ $(H_2O)^+$ complexes.

Under the conditions of our study we found that $C_2H_5Co(DMG)_2(H_2O)$ has k_2 and K_B values of 1.7×10^{-1} M^{-1} sec^{-1} and 4.9 M^{-1}, respectively. Our

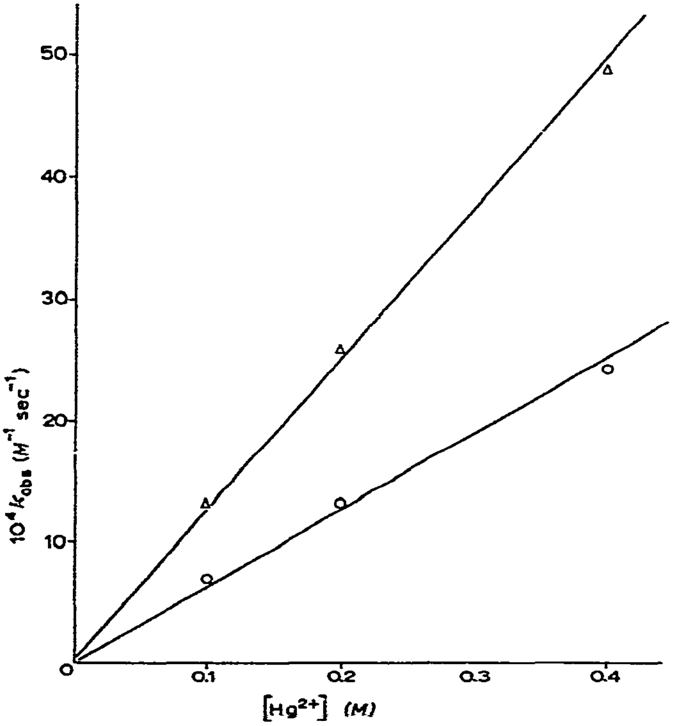


Fig. 2. Representative plots of k_{obs} vs. $[Hg^{2+}]$. ○, n-$C_3H_7Co[BDM(CH_2)_3](H_2O)^+$; △, $C_2H_5Co[BDM(CH_2)_3]$-$(H_2O)^+$.

TABLE 2

KINETIC DATA FOR THE REACTIONS OF $RCo[BDM(CH_2)_3](H_2O)^+$ AND $RCo(DMG)_2(H_2O)$ WITH $Hg(OAc)_2$ [a,b]

R	$RCo[BDM(CH_2)_3](H_2O)^+$ k_2 (M^{-1} sec^{-1}) [c]	$RCo(DMG)_2(H_2O)$ k_2 (M^{-1} sec^{-1})
CH_3	9.2×10^{-3}	6.6×10^{-2} [d]
C_2H_5	4.4×10^{-5}	7.7×10^{-4} [d]
n-C_3H_7	3.1×10^{-5}	7.0×10^{-4} [d]
n-C_4H_9	3.3×10^{-5}	7.2×10^{-4} [e]
$CH_2C_6H_5$	3.9×10^{-5}	7.9×10^{-4} [e]

[a] In a 0.1 M HOAc—0.1 M NaOAc buffer. [b] k_2 obtained from $k_{obs}/[Hg(OAc)_2]$. [c] At 23° C. [d] From ref. 3, at 26° C. [e] Unpublished data at 26° C of G.N. Schrauzer and J.H. Weber.

values are somewhat higher than the k_2 (1.2×10^{-1} M^{-1} sec^{-1}) [4, 5] and K_B (3.9 and 4.2 M^{-1}) [4, 5] values found previously because of the different reaction conditions including higher ionic strength. A major point of interest is that the reaction of $C_2H_5Co[BDM(CH_2)_3](H_2O)^+$ is ten times slower than the reaction of $C_2H_5Co(DMG)_2(H_2O)$. This occurs because the cationic complex is less susceptible to a bimolecular electrophilic attack than a very similar neutral complex.

The studies done in the HOAc—NaOAc buffer with a $Hg(OAc)_2$ electrophile source generally support the above conclusions (Table 2). The reactions are slower in the acetate system than in the perchlorate system by an average factor of 350 because of the high stability of $Hg(OAc)_2$ and the resulting low $[Hg^{2+}]$ [11]. Possibly the attacking electrophile is $HgOAc^+$. The reaction rates of the $BDM(CH_2)_3$ complexes average about 17 times slower than the rates of the DMG complexes for the same alkyl groups. The order of k_2 values for both systems is: $CH_3 \gg C_2H_5 \simeq CH_2C_6H_5 \simeq$ n-$C_3H_7 \simeq$ n-C_4H_9. The relative rates between the two systems and among the R groups in each system further corroborate the S_E2 mechanism with a direct attack on the cobalt—carbon bond by a mercury electrophile.

Experimental

The analytical data of the products obtained are given in Table 3.

Preparation of $Co[BDM(CH_2)_3]Br_2$

The dibromo complex was prepared by modifying the method of Costa, Mestroni, and de Savorgnani [12]. The ligand was prepared [13] in sufficient quantity for a theoretical yield of 70 g (0.15 mole). The crude ligand, separated by evaporating the benzene, was dissolved in 800 ml of acetone. $CoBr_2 \cdot 6H_2O$ (60 g, 0.18 mole) was added, and the product was formed by bubbling air through the solution for several hours. The product was recrystallized from acetone/water (30/1, v/v) and vacuum dried at room temperature resulting in a 47% yield.

Preparation of $RCo[BDM(CH_2)_3](H_2O)^+$ complexes and $C_2H_5Co[BDM(CH_2)_2]$-$(H_2O)^+$

The CH_3, C_2H_5, n-C_3H_7, and n-C_4H_9 complexes of $BDM(CH_2)_3$ were pre-

TABLE 3

ANALYTICAL DATA [FOUND (CALCD.) (%)] OF THE PRODUCTS OBTAINED

Compound	Empirical formula	C	H	N
$Co[BDM(CH_2)_3]Br$	$C_{11}H_{19}Br_2CoN_4O_2$	28.80 (29.33)	4.14 (4.23)	12.20 (11.96)
$[CH_3Co\{BDM(CH_2)_3\}H_2O]ClO_4$	$C_{12}H_{21}ClCoN_4O_7$	32.15 (32.43)	5.36 (5.48)	12.48 (12.64)
$[C_2H_5Co\{BDM(CH_2)_3\}]BF_4$	$C_{13}H_{24}BCoF_4N_4O_2$	37.60 (37.49)	5.79 (5.77)	13.55 (13.68)
$[n\text{-}C_3H_7Co\{BDM(CH_2)_3\}H_2O]BF_4$	$C_{14}H_{28}BCoF_4N_4O_3$	37.68 (37.53)	6 33 (6.17)	12.68 (12.29)
$[n\text{-}C_4H_9Co\{BDM(CH_2)_3\}]BF_4$	$C_{15}H_{28}BCoF_4N_4O_2$	40.70 (41.01)	6 59 (6.70)	12.68 (12.56)
$[C_6H_5CH_2Co\{BDM(CH_2)_3\}H_2O]ClO_4$	$C_{18}H_{28}ClCoN_4O_7$	42.75 (42.75)	5.53 (5.47)	11.07 (11.07)
$[C_2H_5Co\{BDM(CH_2)_2\}]BF_4$	$C_{12}H_{22}BCoF_4N_4O_2$	36.02 (35.72)	5.54 (5.47)	14.00 (13.51)
$Co[BDM(CH_2)_3BF_2]Br_2$	$C_{11}H_{18}BBr_2CoF_2N_4O_2$	26.05 (26.34)	3.56 (3.60)	11.05 (10.98)
$[CH_3Co\{BDM(CH_2)_3BF_2\}H_2O]ClO_4$	$C_{12}H_{20}BClCoF_2N_4O_7$	30.10 (30.17)	4.81 (4.89)	11.70 (11.58)

pared by the method of Costa et al. [12]. The $C_6H_5CH_2$ derivative was crystallized, after removing interfering halides with $AgClO_4$, by adding $HClO_4$. The brown crystals were obtained after slow evaporation. $[C_2H_5Co\{BDM(CH_2)_2\}H_2O]BF_4$ was prepared by the method of Schrauzer, Sibert, and Windgassen [13]. All samples were dried in a vacuum desiccator at room temperature before analysis.

Preparation of $Co[BDM(CH_2)_3BF_2]Br_2$

This complex was prepared by the method used by Schrauzer and Windgassen [14] to make $CH_3Co(DMGBF_2)_2H_2O$. $Co[BDM(CH_2)_3]Br_2$ (1 g, 0.00218 mole) was mixed with 75 ml of diethyl ether and an excess of boron trifluoride diethyl ether (10 ml, 45% BF_3) was added. The heterogeneous mixture was stirred for several hours, and the grey-green product was separated by filtration. The crude product was recrystallized from acetone/water (30/1, v/v).

Preparation of $[CH_3Co\{BDM(CH_2)_3BF_2\}H_2O]ClO_4$

$Co[\{BDM(CH_2)_3\}BF_2]Br_2$ (5.55 g, 0.01 mole) was added to 100 ml of aqueous methanol (1/10, v/v) and the solution was deaerated with nitrogen. CH_3I (1.60 g, 0.011 mole) and an aqueous solution of $NaBH_4$ (0.2 g, 0.0055 mole) were added in succession. Additional $NaBH_4$ was added next until all the $Co[BDM(CH_2)_3BF_2]Br_2$ dissolved. The solution was filtered and acetone was added. Upon cooling to 0° C, a reddish-orange solid settled out. The solid, which contained I^-, was purified by dissolving it in acetone and adding an aqeous solution of $AgClO_4$. After filtering off the silver halides, an aqueous solution of $NaClO_4$ was added. Slow evaporation yielded pure reddish-orange crystals.

Kinetics and data treatment

The reaction kinetics were followed spectrophotometrically at 460 nm ($R = CH_3$) or at 480 nm (other R) using a Cary 14 spectrophotometer at 25.0° C. The extinction coefficient drops from an approximate 2.2×10^2 value for the reactants to nearly zero for $Co(BDMBg)(H_2O)_2^{2+}$. Most of the reactions were carried out in water containing 1.0 *M* $HClO_4$ and a $Hg(ClO_4)_2$ concentration ranging from 0.01 to 0.4 *M*. The ionic strength of the solutions was maintained at 2.2 by adding $NaClO_4$ when necessary. Other reactions were studied at 23°C in a 0.1 *M* acetic acid—0.1 *M* sodium acetate buffer using 0.1 *M* $Hg(OAc)_2$ as the electrophile source.

The data were analyzed using a least squares computer program. A regression analysis was performed to obtain k_2 and k_{obs} values. The correlation coefficients generally varied from 0.998 to 1.000.

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