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KINETICS OF TRANSFER OF COORDINATED CARBANIONS FROM COBALT TO MERCURY(II) IN TWO FAMILIES OF MODEL VITAMIN B12 COMPOUNDS

G TAUZHER, R. DREOS, G COSTA
Istituto di Chimica, Università di Trieste, Trieste (Italy)
and MICHAEL GREEN*
Department of Chemistry, University of York, York (Great Britain)

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Summary

Intermediates are revealed by kinetic studies on the transalkylation by mercury(II) of alkyl- and aryl-aquo-1,3-bis(diacetylmonoximeimino)propanatocobalt(III) mono cations and of alkylaquo-*N*,*N*′-ethylenebis(salicylideneiminato)-cobalt(III).

Transfer of the alkyl group to Hg^{2+} from alkylcobalt corrinoid compounds [1—3, 5] and various alkylaquobis(dimethylglyoximato)cobalt complexes [4, 6, 7] (cobaloximes) appears to involve one simple step (eqn. 1). In some cases,

$$RM + Hg^{2+} \rightarrow M^+ + RHg^+ \qquad (1)$$

(R = alkyl, M = cobalt complex less R, i.e. cobalt + extended equatorial ligand + usually, one axial ligand, RM may be charged)

the kinetics are more complicated than implied by eqn. 1, but this is due to side reactions, e.g coordination of Hg^{2+} to benzimidazole in the cobalamins [3], and protonation in the cobaloximes [7], as in eqn 2. We are reporting the reactions of two related cobalt systems, where in contrast to the simple process 1, evidence is found for two steps involving the formation of intermediates, $RMHg^{2+}$

$$RM + H^+ \rightleftharpoons RMH^+ \qquad (2)$$

An investigation has been made of the kinetics of dealkylation and dearylation by the mercury(II) ion of $[RCo\{(DO)(DOH)pn\}H_2O]^+$ (I) and of dealkylation of $RCo(salen)H_2O$ (II) in water. (Using the earlier rotation, RM carries a charge of +1 in the first case and 0 in the second). The reactions were followed spectro-

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* For correspondence

photometrically using stopped flow techniques where necessary. In every case studied, graphs of rate against $[Hg^{2+}]$ curved from linearity at high concentrations of the latter, while strictly linear relationshipe were obtained between the reciprocals of these quantities. Reactions 3 and 4 are postulated.

$$RM + Hg^{2+} \rightleftharpoons RM \cdot Hg^{2+} \qquad (3)$$

$$RM \cdot Hg^{2+} + H_2O \rightarrow MH_2O^+ + RHg^+ \qquad (4)$$

If $K_3 = k_3/k_{-3}$ and if $k_4 \ll k_3$ then

$$\frac{-d[RM]}{dt} = \frac{k_4K_3\,[RM]\,[Hg^{2+}]}{1 + K_3[Hg^{2+}]}$$

which is completely compatible with observations for $[RCo\{(DO)(DOH)pn\}H_2O]^+$. In studying these compounds $[H^+]$ was varied from 0.025 to 0.7 M, but no evidence was found of protonation to $[RCo\{(DOH)(DOH)pn\}H_2O]^{2+}$ or of retardation of reaction due to process 2 taking place, as observed in the dealkylation of cobaloximes [7] and of $RCo(salen)H_2O$ (see below).

In the case of the $RCo(salen)H_2O$ compounds, an inverse dependence on acidity was also observed, the reciprocal of the rate being proportional to $[H^+]$ on the basis of which reaction 2 is included. Then, working as before.

$$\frac{-d[RM]}{dt} = \frac{k_4K_3[RM]\,[Hg^{2+}]}{1 + K_2[H^+] + K_3[Hg^{2+}]}$$

which described fully the kinetics for $RCo(salen)H_2O$

The production of MH_2O^+ was verified spectrophotometrically, and that of the RHg^+ species by means of the melting points of chlorides and/or iodides precipitated from concentrated reaction mixtures with excess halide ion. Tables 1 and 2 contain the data on the RM compounds and also a fluoroboron derivative, $[CH_3Co\{(DO)(DOBF_2)pn\}H_2O]^+$, in which BF_2 replaces H. In forming a detectable intermediate, namely $RM \cdot Hg^{2+}$, the systems here contrast with the cobalt corrinoids and cobaloximes mentioned earlier [1—8]. (Chloromethylcobaloxime forms a very stable complex with Hg^{2+} but it is different [7] in being destroyed by a second mercury(II) ion.) In the other systems [2, 6, 7] upper limits can be placed in possible K_3 terms of about 0.03 M^{-1}, if it is assumed that the highest concentrations of Hg^{2+} used in them (see ref. 6, in which highest $[Hg] = 1\ M$) were comparable to those used here (see footnotes to Tables). The values of K_3 for I and II are considerably larger.

TABLE 1

DATA FOR $[RCo\{(DO)(DOH)pn\}H_2O]^{+\,a}$

R	K_3 (M^{-1})	k_4 (sec^{-1})	K_3k_4 ($M^{-1}\ sec^{-1}$)	n
Me	1.18 ± 0.11	1.33 ± 0.11	1.56 ± 0.01	35
Et	1.38 ± 0.13	0.00422 ± 0.00033	0.00585 ± 0.00006	8
n-Pr	0.73 ± 0.17	0.00400 ± 0.00085	0.00291 ± 0.00005	10
$PhCH_2$	2.41 ± 0.49	0.00159 ± 0.00029	0.00383 ± 0.00009	7
Ph	2.91 ± 0.45	1.31 ± 0.22	3.82 ± 0.05	43
Me (BF_2 derivative)	3.19 ± 0.21	0.000218 ± 0.000010	0.00066 ± 0.00001	6

[a] Temperature 25.0 ± 0.1°, except for BF_2 derivative (40.0 ± 0.1°) ionic strength 1 M (using $NaClO_4$ or $HClO_4$), $2 \times 10^{-4}\ M \leq [RM] \leq 4 \times 10^{-4}\ M$, $0.01\ M \leq [Hg^{2+}] \leq 0.3\ M$, data obtained by least squares regressions, errors are standard deviations, n is number of sets of observations

TABLE 2

DATA FOR RCo(salen)H_2O [a]

R	K_3 (M^{-1})	k_4 (sec^{-1})	K_3k_4 (M^{-1} sec^{-1})	K_2	n
Me	376 ± 42	83.7 ± 2.6	31500 ± 3700	20.6 ± 2.3	54
Et	351 ± 80	0.240 ± 0.019	84 ± 20	21.3 ± 4.7	28

[a] Temperature 25.0 ± 0.1°, ionic strength 1 M (using $NaClO_4$ or $HClO_4$), 2×10^{-4} $M \leq [RM] \leq 4 \times 10^{-4}$ M 0.005 $M \leq [Hg^{2+}] \leq 0.05$ M 0.026 $M \leq [H^+] \leq 0.49$ M, data obtained by least squares multiple regressions, errors are standard deviations, n is number of sets of data

Transmethylation occurs much more readily than transfer of other alkyl groups in the corrinoid and cobaloxime systems. The term K_3k_4 here is equivalent to k_1 in them. Like k_1, for the corrinoids and cobaloximes, K_3k_4 reflects the ease of transalkylation or transarylation. the [RCo{(DO)(DOH)pn}H_2O]$^+$ systems follow the cobaloximes [9] Ph > Me > Et > n-Pr ≈ $PhCH_2$.

In the case of C_2H_5Co(salen), by working with a saturated water—methanol solution containing chloride ion, a green product C_2H_5Co(salen)$HgCl_2$ was obtained (Found: C, 34.4; H, 3.0; N, 4.65. Calcd: C, 34.05; H, 3.0; N, 4.4%.)

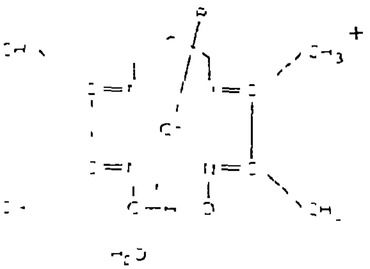
From a kinetic point of view, reaction 4 could be replaced by 5.

$$RM + Hg^{2+} \rightarrow RHg^{+} + MH_2O^{+} \qquad (5)$$

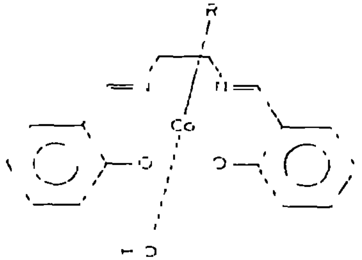
Working as before, reactions 2, 3 and 5 lead to

$$\frac{-d[RM]}{dt} = \frac{k_5[RM][Hg^{2+}]}{1 + K_2[H^+] + K_3[Hg^{2+}]}$$

This scheme assumes that the formation of RM·Hg^{2+} does not lead to dealkylation implying that the mercury atom is too remote from R to result in a reaction. This is plausible for methylcobalamin where there would be serious steric difficulties in moving Hg^{2+} from the benzimidazole to the methyl group (cf. step 1 of DeSimone et al. [3]). However, it seems extremely unlikely in the present systems where it is difficult to imagine what free energy factors could prevent migration of Hg^{2+} from an O atom to CH_3 group, for example.



(I)



(II)

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