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CLEAVAGE BY HALOGENS OF CARBON—COBALT BONDS IN ORGANOMETALLIC COMPLEXES OF COBALT(III)

IV *. KINETICS AND MECHANISM OF THE REACTIONS OF ORGANOBIS(DIMETHYLGLYOXIMATO) COBALT (III) COMPLEXES WITH IODINE IN METHANOL

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Summary

The mechanism of the reaction between the organocobaloximes RCo-$(DH)_2H_2O$ (DH = dimethylglyoximate) and iodine in methanol has been studied and a comparison made with the corresponding reaction in chloroform. The effect of the solvent on the reaction mechanism and the role of nucleophilic assistance are discussed.

Introduction

In a previous paper in this series [1] we described a study of the mechanism of the reaction between organocobaloximes and iodine in chloroform. In order to examine the effect on the reactivity and on the mechanism of change from a non-coordinating to an oxygenated polar solvent, we have now examined the reaction in methanol Electrophilic substitutions are generally strongly affected by the solvent, as is evident from data on organometallic compounds of Hg, Pb, Sn, which have been most extensively studied [2,3,4].

Results

The reaction examined was:

$$RCo(DH)_2H_2O + I_2 \rightarrow RI + ICo(DH)_2H_2O$$

(R = CH_3, C_2H_5, n-C_3H_7, i-C_3H_7, CH_2Cl)

* For Part III see ref. 1.

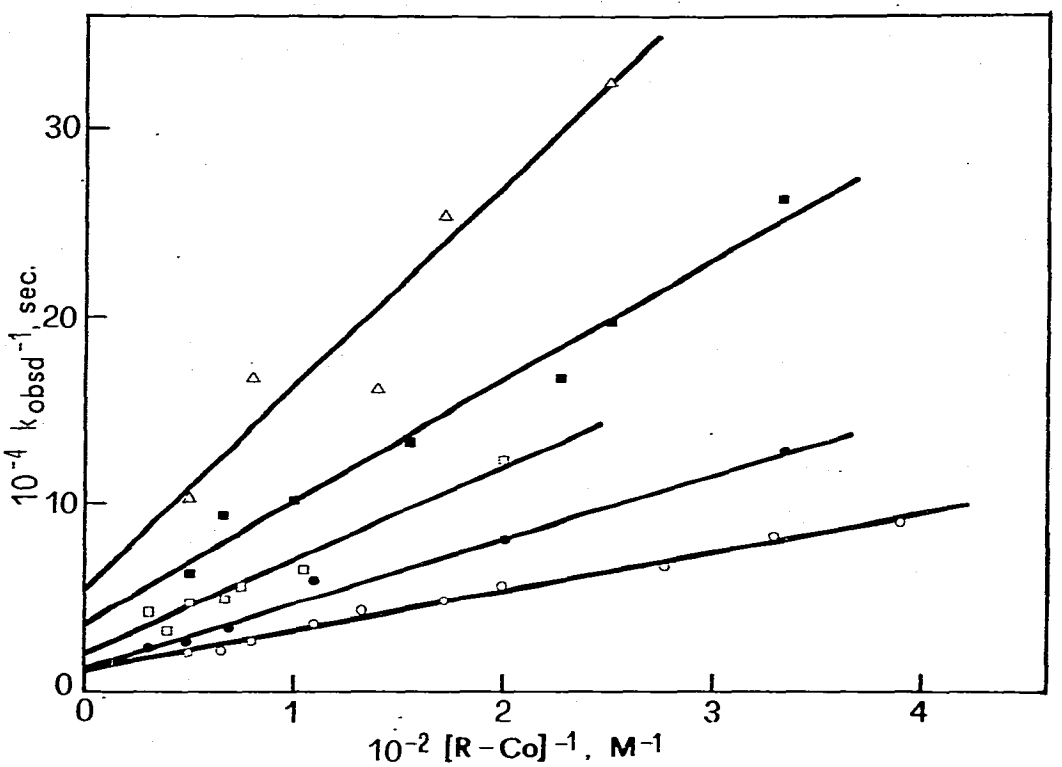


Fig. 1. Plots of the reciprocal of the pseudo first order k_{obsd} vs. $[RCo]^{-1}$, for R = CH_3 (○), C_2H_5 (□), nC_3H_7 (■), iC_3H_7 (●), CH_2Cl (△).

The products from the reaction in methanol at room temperature were determined, the alkyl halides being identified by GLC and the iodocobaloximes by elemental analysis. Kinetic measurements were carried out in methanol at 25°C.

As for the reactions in chloroform [1], the progress of the interaction cannot be monitored spectrophotometrically owing to the strong absorption of both reagents over the whole accessible UV—visible region, and so the rate constants were determined by titration (with $Na_2S_2O_3$) of the remaining iodine in solutions containing an excess of the complex. In every case the pseudo first order

TABLE 1

RATE AND PRE-EQUILIBRIUM CONSTANTS FOR THE REACTION BETWEEN $RCo(DH)_2H_2O$ AND I_2 [a]

R	$10^3 k_{2a}$(mol^{-1} s^{-1})	K_a(mol^{-1})	n	10^2[RCo] (mol)	$10^3 k_2$(mol^{-1} s^{-1}) [b]
CH_3	4.85 ± 0.17	59.3 ± 7.9	10	0.25—2.00	19.93 ± 0.82
C_2H_5	2.02 ± 0.20	41.7 ± 10.3	7	0.5 —3.00	7.43 ± 1.88
n-C_3H_7	1.55 ± 0.11	56.5 ± 14.1	7	0.3 —2.00	0.69 ± 0.72
i-C_3H_7	2.84 ± 0.13	33.5 ± 7.03	6	0.3 —3.00	11.2 ± 1.5
CH_2Cl	0.93 ± 0.17	50.6 ± 30.7	5	0.5 —2.5	5.65 ± 1.47

[a] Temperature 25 ± 0.1°C, solvent methanol, except for k_2 (solvent chloroform). Data obtained by least squares regressions, errors are standard deviations, n is number of sets of observations. [b] From ref. 1.

rate plots were linear over a large proportion of the reaction. The graph of k_{obsd} versus [RCo] shows deviations from linearity as the complex concentration increases, but a linear relationship is obtained between the reciprocals of these quantities. (Fig. 1) Thus equation 1 applies:

$$k_{obsd} = \frac{k_{2a}[RCo]}{1 + K_a[RCo]} \quad (1)$$

The k_{2a} and K_a values are listed in Table 1.

Discussion

The comparison of the expression (1) with that obtained for k_{obsd} in chloroform [1]

$$k_{obsd} = \frac{k_2[RCo]}{1 + K[RCo]} + \frac{k_3[RCo]^2}{1 + K[RCo]} \quad (2)$$

suggests that in both solvents the reaction mechanism involves a pre-equilibrium, but in methanol the term depending on $[RCo]^2$ is absent. The pre-equilibrium in both cases involves the formation of 1/1 adduct between the organometallic and iodine

$$RCo(DH)_2H_2O + I_2 \overset{K_a}{\rightleftharpoons} RCo(DH)_2H_2O \cdot I_2 \quad (3)$$

The rate determining step may consist of the intramolecular transalkylation

$$RCo(DH)_2H_2O \cdot I_2 \xrightarrow{k'_{2a}} \text{products} \quad (4)$$

with $k_{2a} = k'_{2a}K_a$

or of the reaction between organocobaloxime and free iodine

$$RCo(DH)_2H_2O + I_2 \xrightarrow{k''_{2a}} \text{products} \quad (5)$$

with $k_{2a} = k''_{2a}$

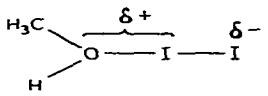
We have previously discussed the evidence in favour of step 4 instead of step 5 for the reaction in chloroform [1]; in methanol the available data do not permit a choice to be made.

Quantitative comparison cannot be made between the pre-equilibrium constants in chloroform (K) and those in methanol (K_a) In chloroform a numerical value could be obtained only for R = CH_2Cl ($K = 122 \pm 50\ M^{-1}$), for which $K > K_a$. However for all the other complexes an upper limit of about $10\ M^{-1}$ can be estimated for K, so that for these complexes $K_a > K$ (Table 1). The increase in the pre-equilibrium constants passing from chloroform to methanol is consistent with the hypothesis that in the complex $RCo(DH)_2H_2O.I_2$(I) there is some charge separation, which is stabilized by the polar solvent. From the results in Table 1 it appears that the variations of the K_a values as the R group is changed are within the limits of experimental error, so that no trend can be discussed. The absence of significant variation suggests that complexation occurs at the equatorial chelating ring rather than at the axial position trans to the R group.

When the reaction is carried out in chloroform, complex I acts as an electrophile towards another organometallic molecule

$$RCo(DH)_2H_2O \cdot I_2 + RCo(DH)_2H_2O \xrightarrow{k_3} \text{products} \qquad (6)$$

This gives rise to the third order term (second order in complex, first order in iodine) in the rate expression. This implies that the adduct formation promotes the reactivity of iodine towards nucleophilic centers by placing some positive charge on the halogen, so that complex I may compete with free iodine in the transalkylation reaction, although its concentration in solution is always smaller than that of free iodine ($[RCoI_2]/[I_2]_{free} = K[RCo] < 1$ in chloroform). In methanol the third order term is not evident even at high complex concentrations, where $[RCoI_2]/[I_2]_{free} = K[RCo] > 1$ *; thus in this solvent the bound iodine is a weaker electrophile than the free iodine. The polar oxygenated solvent may solvate one molecule of free halogen as follows [5]:



This would lead to a decrease in the electrophilic power of the reagent. The solvent may solvate the molecule of bound iodine even more strongly, as the latter carries some excess positive charge and this will further decrease the electrophilic activity of the halogen.

Comparison of the k_{2a} with the k_2 values for the reaction in chloroform shows that the rate falls on passing from a nonpolar to an oxygenated polar solvent. In contrast, electrophilic substitution reactions generally have higher rates in polar solvents, as is evident from the data on organometallic compounds of Hg, Pb, Sn and this reactivity increase is ascribed to an enhancement of the nucleophilic assistance. Either the polar solvent itself, or the nucleophilic centre of the electrophile, which carries a greater concentration of negative charge in a polar than in a non polar solvent, may coordinate to the metal atom [2]. This coordination promotes the polarization of the metal—carbon bond in the sense $\overset{+}{M}—\overline{C}$, increasing the ease of reaction and counterbalancing the decreased electrophilic power of the halogen. In the organocobaloximes the coordination to the metal atom would lead to the formation of a heptacoordinated intermediate, which is unlikely for the octahedral complexes of cobalt (III). Thus for these complexes the contribution from nucleophilic assistance must be absent. If the reaction occurs through process 4, the iodine bound to the equatorial chelating ring would again promote the polarization of the carbon—cobalt bond in the sense (δ—) RCo-$(DH)_2H_2O \cdot I_2(\delta+)$ but much less dramatically than if the coordination occured to the metal atom, so that the decreased electrophilic power of the halogen is not counterbalanced. In any case a fall in rate is to be expected passing from chloroform to methanol.

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* For the n-propyl derivative, at $[RCo] > 5 \times 10^{-2}$, the graph of k_{obsd} versus [RCo] shows an increase in the reaction order, which would be consistent with the presence of a third order term in methanol, but at these concentrations the presence of dimers cannot be excluded.

The sequence of k_{2a} in methanol

$CH_3 > i\text{-}C_3H_7 > C_2H_5 > n\text{-}C_3H_7 > CH_2Cl$

is similar to that in chloroform:

$CH_3 > i\text{-}C_3H_7 > C_2H_5 > CH_2Cl > n\text{-}C_3H_7$

except for the chloromethyl derivative, which in methanol is the least reactive. The k_{2a} values vary over a narrower range than in chloroform. The smallness of the effect of the variation of the R group on the rate constants and the high reactivity of the i-propyl derivative in chloroform indicate that the reactions with halogens are less sterically dependent than the corresponding reactions with metal ions. The question whether this behavior is mainly determined by the electrophilic power of the reagent or by the degree of its solvation remains unanswered [1]. Since the variation is smaller in a polar solvent, where the halogen is strongly solvated but its electrophilic power is weaker, it is likely that the selectivity is mainly determined by the strength of the electrophile.

Experimental

The organocobaloximes were prepared as pyridine derivatives [6]. The aquo complexes were obtained by hydrolysis of the pyridinate with dilute $HClO_4$ in methanol. The iodine used was C. Erba bisublimate, and the methanol was C. Erba reagent grade. The alkyl halides were identified by GLC on a 2 m column of Carbowax with a C. Erba Model G.T. gas chromatograph.

The iodine concentrations were measured by potentiometric titrations with a potentiograph Metrohm E 336 equipped with a combined Pt, Ag/AgCl electrode, as described in ref. 1.

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