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ON THE CARBON MONOXIDE ADDUCT FORMATION OF A COBALT-TETRAOXIME COMPLEX

Joseph BACKES, Isao MASUDA, and Koichiro SHINRA
Department of Applied Chemistry, Faculty of Engineering, Osaka University
Yamada-Kami, Suita, Osaka

In a hydrazine hydrate/DMA solution $CoCl_2 \cdot 6H_2O$ and $CH_3C(NOH)C(NOH)\text{-}(CH_2)_{10}\text{-}C(NOH)C(NOH)CH_3$ were found to absorb up to 0.5 mole of CO per 1 mole of cobaltous ion to form a CO adduct which releases CO in air to give a Co(II)-tetraoxime complex. A Co(I)-tetraoxime intermediate is considered to be the reactive species toward CO.

Cobaloximes, as model compounds for Vitamin B_{12} 1), as well as related Co-N_4 type complexes have been investigated previously by Schrauzer et al.2) and by Costa et al.3) as far as their reactivity toward CO is concerned. Schrauzer reported that hydroxy(aquo)- or hydroxy(pyridine)-bis(dimethylglyoximato)Co(III) were inactive toward CO unless a trace of di(aquo)bis(dimethylglyoximato)Co(II) was added. The Co(II)-complex is believed to react with CO at pH 8 - 12 yielding CO_2 and a Co(I)-complex. The latter reduces the Co(III)-complex to the Co(II)-complex.

On the other hand, Costa found that Co(III)-complexes of the type Co^{III}-L [L = 1(diacetylmonoximato)3(diacetylmonoxime-imino)propane monoanion] interact with CO in alkaline solution to give the Co(II)-derivative and CO_2. The above authors propose the formation of an intermediate CO adduct of the Co-complexes. The crystalline [(Co-L)CO] could be isolated by Costa.

In the present study a cobalt complex with the tetraoxime ligand $CH_3C(NOH)C(NOH)\text{-}(CH_2)_{10}\text{-}C(NOH)C(NOH)CH_3$ ($R\text{-}TOH_4$)4) was found to combine with CO at a ratio of Co : CO = 2 : 1 in hydrazine hydrate/DMA solution to form an adduct stable in the presence of CO.

Upon addition of hydrazine hydrate to a solution of $CoCl_2 \cdot 6H_2O$ and $R\text{-}TOH_4$ in DMA, in the complete absence of air, a dark blue-green solution is obtained, which is unstable and rapidly turns brown. The blue-green solution absorbs CO while turning intensely violet; the brown solution is not reactive any more. The volumetric measurements of the CO absorption indicate that for one mole of cobaltous ion up to 0.5 mole of CO are absorbed (Fig. 1). Gas-chromatographic analysis*

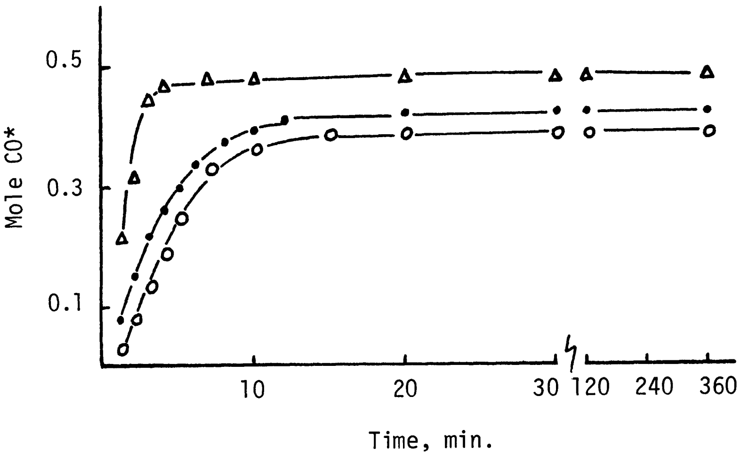

Fig. 1. Volumetric absorption of CO.

(Δ) 1.5 mmol $R\text{-}TOH_4$ + 0.98 mmol $CoCl_2 \cdot 6H_2O$ in 50 ml hydrazine hydrate and 5 ml DMA,

(•) 0.96 mmol $(DmgH)_2Co(OH_2)_2$ in 50 ml hydrazine hydrate and 5 ml DMA,

(○) 5 mmol $DmgH_2$ + 0.91 mmol $CoCl_2 \cdot 6H_2O$ in 50 ml hydrazine hydrate and 5 ml DMA.

* Corrected for standard conditions (273°K, 1 atm.).

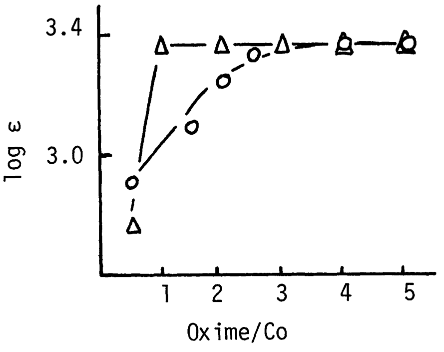

Fig. 2. Absorption intensity of the CO adducts at different oxime/cobalt ratios.

(Δ) $R\text{-}TOH_4$ + $CoCl_2 \cdot 6H_2O$ in 100 ml hydrazine hydrate and 2 ml DMA,

(○) $DmgH_2$ + $CoCl_2 \cdot 6H_2O$ in 100 ml hydrazine hydrate and 2 ml DMA.

of the gas phase at room temperature, 1 atm., after the CO absorption was completed, showed that the concentration of CO was unchanged.

The visible absorption spectrum of the violet solution exhibits a maximum at 17.7 kK with a high extinction coefficient, log ε = 3.35 (Fig. 3). The absorption intensity of the CO adduct for different $Co/R\text{-}TOH_4$ ratios shows that a constant absorption is obtained for a 1 : 1 ratio (Fig. 2). The CO adduct is thus believed to involve a planar $Co\text{-}N_4$ structure where the four oxime groups are coordinated to the metal ion.

An intensely colored CO adduct with an absorption maximum at 18.1 kK is also obtained upon replacing $R\text{-}TOH_4$ by dimethylglyoxime ($DmgH_2$) (Fig. 3); however the expected $DmgH_2$ / Co ratio of 2 : 1 cannot be clearly assessed (Fig. 2). No reactivity toward CO could be observed when using tetraoxime ligands with aromatic linkages$^{4)}$ or α-benzildioxime.

Di(aquo)-bis(dimethylglyoximato)Co(II)$^{5)}$ was found to undergo a similar reaction with CO in hydrazine hydrate/DMA solution (Fig. 1). This behaviour is consistent with the above assumption that the CO adduct includes the $Co\text{-}N_4$ unitary structure.

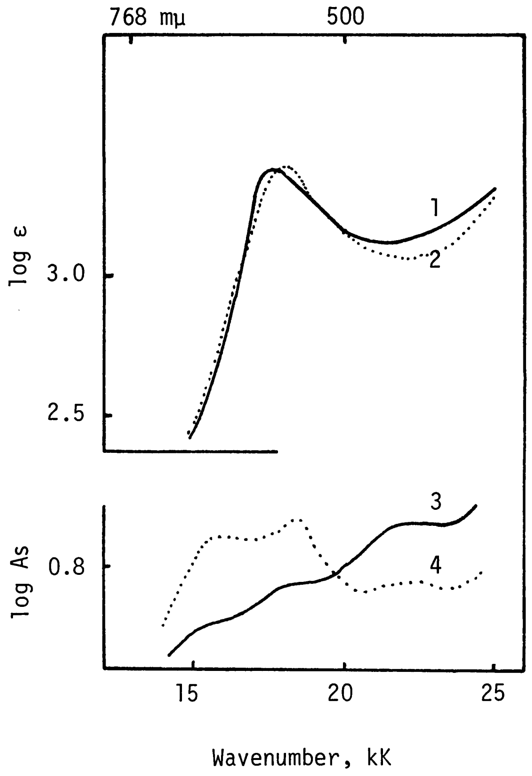

Fig. 3. Electronic absorption spectra of the Co-complexes.

(1) 2.38 mmol R-TOH_4 and 0.47 mmol $CoCl_2 \cdot 6H_2O$ in 100 ml hydrazine hydrate and 2 ml DMA in presence of CO,

(2) 2.45 mmol $DmgH_2$ and 0.49 mmol $CoCl_2 \cdot 6H_2O$ in 100 ml hydrazine hydrate and 2 ml DMA in presence of CO,

(3) R-TOH_4 and $CoCl_2 \cdot 6H_2O$ in hydrazine hydrate,

(4) $DmgH_2$ and $CoCl_2 \cdot 6H_2O$ in hydrazine hydrate.

Though the instability of the earlier mentioned blue-green solutions did not permit quantitative absorption measurements, the absorption pattern with maxima at ca. 22, 19 and 17 kK (Fig. 3) is quite consistent with those of the Co(I)-complexes obtained by the reduction of bis(dimethylglyoximato)Co(II) compounds with H_2, for which a planar Co-N_4 structure with an axial base in the fifth coordination sphere has been postulated.$^{6)}$

The R-$TOH_2 \cdot$Co(II) complex could not be oxidized in air; when applying a general procedure for the preparation of $[Co^{III}(DmgH)_2(Base)_2]^+$ type complexes,$^{7)}$ only a complex corresponding to the formula R-$TOH_2 \cdot$Co(II) was obtained (Found : C, 47.75; H, 6.64; N, 13.75%. Calcd for $C_{16}H_{28}N_4O_4Co$: C, 48.11; H, 7.06; N, 14.03%. The compound is paramagnetic, μ_{eff} = 2.01 B.M. by the Gouy method. A structure similar to the one of the iron(II)-complexes with R-TOH_4 analogues$^{4)}$ is assumed.). In hydrazine solution the oxydation of Co(II) to Co(III) is quite improbable.$^{5,8)}$ In fact no Co(III) species could be detected in the hydrazine solution by polarographic analysis.

On the basis of the above results, a Co(I)-oxime intermediate is believed to interact with CO to form the stable adduct. With reference to the results obtained by Costa$^{3)}$ a 1 : 1 adduct of Co : CO is believed to be formed in solution. The following process is proposed: (see below).

A detailed mechanism leading to the Co(I)-oxime intermediate cannot be given so far.

$$2\ \text{R-}TOH_4 \quad + \quad 2\ Co^{2+} \xrightarrow{\text{in } NH_2NH_2 \cdot H_2O/DMA} Co(I) \quad + \quad Co(II) \qquad (1)$$

$$Co(I) \quad + \quad CO \xrightarrow{\qquad\qquad} Co\text{-}CO \qquad (2)$$

No evidence for the disproportion reaction6) 2 Co(II) $\rightleftharpoons$ Co(I) + Co(III) could be found. However, the presence of the oxime ligand in hydrazine solution is necessary to stabilize this Co(I)-complex. Further stabilization is obtained through the formation of the CO adduct (2). The violet CO adduct in hydrazine solution dissociates molecular CO in vacuo or in air. Upon standing the solution in air, R-TOH_2·Co(II) (Found : C, 47.19; H, 6.91; N, 14.64%) precipitates. The IR spectrum is identical with the one of the R-TOH_2·Co(II) compound described above.

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* Column: 4 mm i.d. x 3 m long; column temp.: 20°C; column packing: molecular sieve 13X; carrier gas: H_2, 120 ml/min.

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