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Preliminary communication

COBALT(II)-TETRACARBONYLCOBALTATE ION PAIRS: ELECTRON TRANSFERS PHENOMENA

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Summary

The disproportionation of $Co_2(CO)_8$ in THF takes place only when water is present. Ion pairing interactions between Co^{2+} and $Co(CO)_4^-$ are observed. The disproportionation is reversible at room temperature and under low P_{CO} as a consequence of electron transfers between Co^{-I} and Co^{II}.

Edgell [1] proved the presence of ion pairs among tetracarbonylcobaltate anion and Group IA cations in THF solutions. On the other hand there are several unquestioned reports that THF promotes the disproportionation of $Co_2(CO)_8$ (I) (eq. 1) [2]:

$$3/2\ Co_2(CO)_8 \xrightarrow{THF} 2Co(CO)_4^- + Co^{2+} + 4CO \qquad (1)$$

It was thus to be expected that in THF solutions tetracarbonylcobaltate could act as a ligand in the coordination sphere of Co^{2+} and this prompted us to investigate the chemical consequences of such an interaction whereby two atoms of the same metal in different oxidation states are held together.

In conflict with the previous reports [2] we found I to be stable in THF: no gas evolution and no change in the IR spectrum (ν(CO): 2070vs, 2040vs with a sh., and 1846 cm^{-1}) were observed during one day at 23°C under a P_{CO} of 595 mmHg. As a result of prolonged gas removal from these solutions $Co_4(CO)_{12}$ (II) is slowly formed, as indicated by the appearance of new characteristic IR bands (ν(CO): 2066vs, 2054vs and 1858s cm^{-1}).

Upon adding small amounts of water to the solutions, however, disproportionation of I occurs, to an extent depending both on H_2O/I molar ratio and on the

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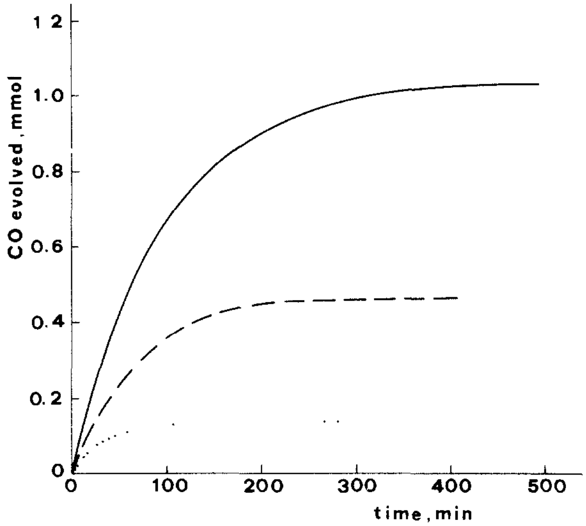


Fig. 1. CO evolved upon addition of water to THF solutions of I. Reaction conditions: 25 ml of 0.03 *M* solution of I in THF; *T* 23°C; P_{CO} 595 mmHg; $H_2O/I = 1$ ......; $H_2O/I = 2$ - - - - -; $H_2O/I = 3.85$ ——.

P_{CO}. Gas volumetric determinations and IR spectroscopy on 0.03 *M* THF solutions of I at various H_2O/I molar ratios in the range 1—3.85 substantiate this finding. The amount of CO evolved (Fig. 1) is not directly proportional to the added water, the molar ratio $CO_{evolved}/H_2O_{added}$ being 0.19 for $H_2O/I = 1$, 0.32 for $H_2O/I = 2$, and 0.39 for $H_2O/I = 3.85$. On decreasing the concentration of added water a higher percentage of it remains inactive in promoting the disproportionation of I.

Preliminary IR investigations on dilute solution of water (0.02—0.1 *M*) in THF showed the presence of two bands at 3570 and 3510 cm^{-1}, conforming to the Lambert—Beer law, which are characteristic of "free" water in THF, and allow its determination. When various amounts of anhydrous $CoCl_2$ are added to the solution, the two bands decrease or disappear altogether, while broad absorptions appear in the range 3450—3150 cm^{-1} as a result of the coordination of water to Co^{2+}. Analogous behaviour is observed during the experiments depicted in Fig. 1, suggesting that water acts as a ligand in the coordination sphere of Co^{2+} produced by the disproportionation of I. At the end of the CO evolution, however, free water is still present in solution (bands at 3570 and 3510 cm^{-1}). The $H_2O_{coordinated}/Co^{2+}$ molar ratios were 4.0 for $H_2O/I = 3.85$, 1.9 for $H_2O/I = 2$ and 0.36 for $H_2O/I = 1$ (The difference between the total and coordinated water was estimated by comparison of IR spectra; the concentration of Co^{2+} was estimated from the amount of CO evolved assuming the stoichiometry of eq. 1). These findings suggest that some other ligand competes with water in the coordination sphere of Co^{2+} and the competition is more efficient at low H_2O_{added}/I ratios. On the other hand, new bands in the 1855—1910 cm^{-1} range, in addition to those of unreacted I, are present at the end of the reaction. At a H_2O/I ratio of 3.85, while there is a hint of a trace of a second species, the absorption is predominantly confined to a single band at 1887 cm^{-1} indicative of a THF symmetrically surrounded $Co(CO)_4^-$ anion. At a H_2O/I ratio of 1, contact ion pairs are formed, as shown by appearance of bands at 1855 (a shoulder in the 1845 cm^{-1} band of I) and 1895 cm^{-1}. At low H_2O/I ratios $Co(CO)_4^-$ may compete with water around Co^{2+}. In this situation, assuming a coordination number of 6 for Co^{2+}, since the $H_2O_{coordinated}/Co^{2+}$ ratio is 0.36 and the esti-

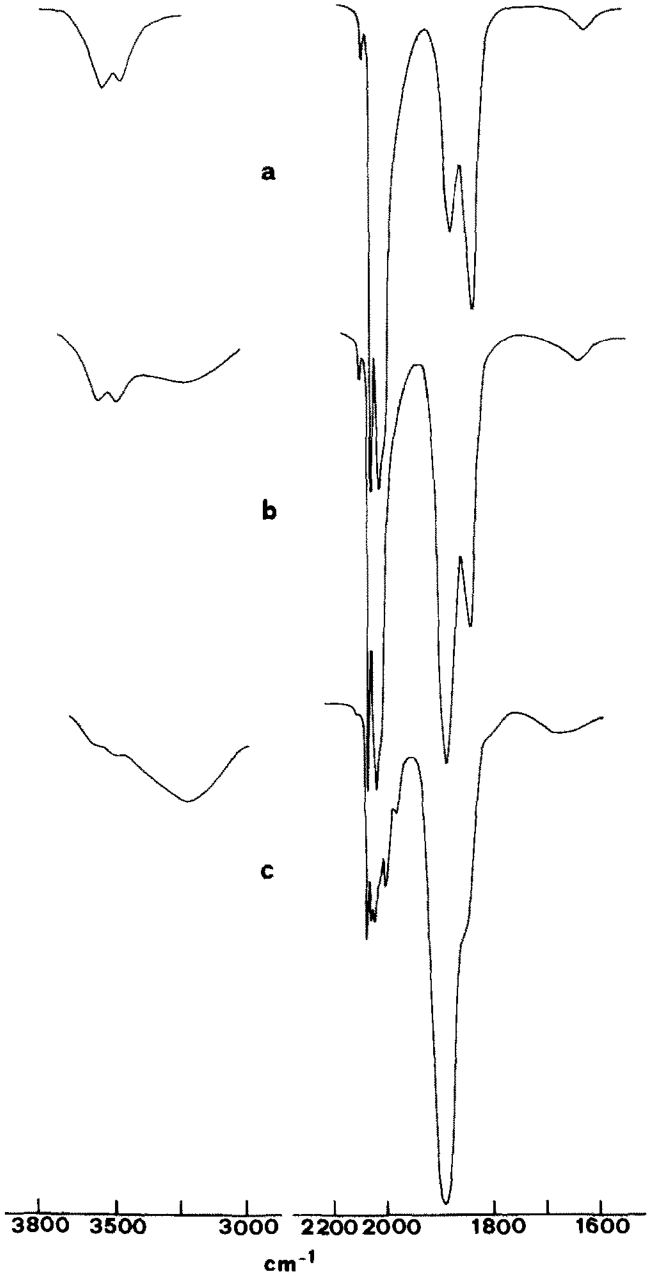


Fig. 2. IR spectra of a 0.03 *M* THF solution of I with $H_2O/I = 2$; (a) immediately after the addition of water, (b) at the end of CO evolution (P_{CO} 595 mmHg), (c) at the end of CO evolution (P_{CO} 40 mmHg). IR absorptions of the solvent have been subtracted.

mated extent of ion pair formation is about 30% [1], a substantial contribution of THF in binding of Co^{2+} can be expected. The difference between the IR spectrum ($H_2O/I = 2$) taken immediately after the addition of water (Fig. 2, spectrum a) and that at the end of the CO evolution (Fig. 2, spectrum b) confirms these ideas.

At a constant H_2O/I molar ratio of 2 lowering the CO pressure to 40 mmHg gives a markedly different IR spectrum (Fig. 2, spectrum c): (i) The bands of I are absent and those of free water almost absent.

(ii) The $Co(CO)_4^-$ bands increase in intensity and new bands appear at 1955 and 1977 cm^{-1}; these new bands are strongly modified by dilution with anhydrous THF and can be ascribed to some complex association phenomena between Co^{2+} and $Co(CO)_4^-$ (i.e. triple ions).

(iii) Low intensity bands due to small amounts of $Co_4(CO)_{12}$ are present.

On restoring the original CO pressure at 595 mmHg, absorption of gas takes place at room temperature and in a few minutes the IR spectrum of the solution becomes identical to that shown in Fig. 2, spectrum b. This indicates that under these conditions II is readily converted into I. Independent experiments confirm that in wet THF solutions II is converted into I at room temperature under one atmosphere pressure of CO.

The results show that:

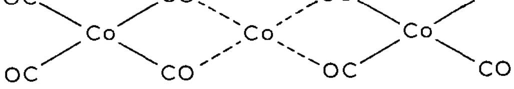
(i) The occurrence of reaction 1 is brought about by the presence of water and in absence of water no disproportionation is observed.

(ii) Co^{2+} produced in reaction takes up THF, H_2O and $Co(CO)_4^-$ as ligands in complex equilibria.

(iii) Ion pairing interactions between Co^{2+} and $Co(CO)_4^-$ take place in 0.03 M solution at a H_2O/I molar ratio in the range 1—3.85 and at P_{CO} of 40—595 mmHg.

(iv) Under the conditions used reaction 1 is reversible as a consequence of electron transfers between Co^{-I} and Co^{II}.

The electron transfers can be viewed as the consequence of an intimate ion pair association between Co^{2+} and $Co(CO)_4^-$. Such association may involve various species, including that shown in formula A, in which the $Co(CO)_4^-$ is acting as a bidentate ligand for Co^{2+}. This model provides a simplified representation how the electron transfer, mediated by the CO ligand, can occur between the two cobalt ions. The Co^0 species so formed is expected to have a high affinity for carbon monoxide.



(A)

Experimental

THF was distilled from $LiAlH_4$ and handled under prepurified Argon. $Co_2(CO)_8$ (Strem Chemicals) was purified by sublimation. IR spectra were recorded on a Perkin—Elmer 983 spectrophotometer using CaF_2 0.01 mm thickness cells.

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