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Kinetics and Mechanism of the Decomposition of Dicobalt Octacarbonyl to Tetracobalt Dodecacarbonyl and Carbon Monoxide

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The decomposition of dicobalt octacarbonyl, dissolved in toluene, to tetracobalt dodecacarbonyl and carbon monoxide can be described by the kinetic equation

$$\frac{-d[Co_2(CO)_8]}{dt} = k[Co_2(CO)_8]^2(p_{CO})^{-4}$$

This supports a mechanism according which the rate determining step is the dimerization of $Co_2(CO)_6$ fragments formed from $Co_2(CO)_8$ by loss of two carbon monoxide ligands.

Introduction

The chemistry of metal carbonyl clusters has received considerable attention in recent years.[1] This attention was focused mainly on the preparative and structural aspects of these complexes and no information is available up till now on the mechanism of metal carbonyl cluster formation.

The thermal decomposition of $Co_2(CO)_8$ to obtain $Co_4(CO)_{12}$ was employed first in 1910[2] and later refined[3] to achieve better yields. The equilibrium constant of the reaction

$$2Co_2(CO)_8 \rightleftharpoons Co_4(CO)_{12}+4CO$$

was determined,[4] but no kinetic measurements were made.

Results and Discussion

The decomposition of $Co_2(CO)_8$ to $Co_4(CO)_{12}$ was studied at 1 atm total pressure in toluene solution in the temperature range between 40 and 61°C, at different carbon monoxide partial pressures. The reaction was found to be irreversible under the conditions used and the surface of the glass vessel had no influence on the reaction rate.

The reaction was followed by measuring the volume of gas evolved. Since above 50°C slow decomposition of $Co_4(CO)_{12}$ was already noticeable (probably metallic cobalt is formed but due to the small amounts involved this could not be proved exactly), the gas volume measured had to be corrected for this secondary reaction to get reliable results. This was achieved by separately determining the rate of $Co_4(CO)_{12}$ decomposition and applying these data at the actual concentrations of $Co_4(CO)_{12}$ in the reaction mixtures. The decomposition of $Co_4(CO)_{12}$ was only slightly influenced by the carbon monoxide partial pressure, as shown in Figure 1. This circumstance simplified the calculations for the necessary correction.

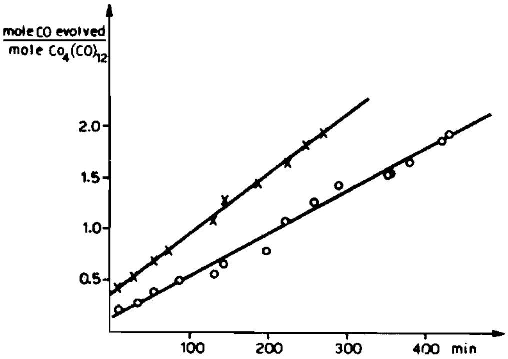

Figure 1. Decomposition of $Co_4(CO)_{12}$, dissolved in toluene, at 61°C and 1 atm. Concentration of $Co_4(CO)_{12}$ solution: 0.023 mmole/ml × × × N_2 atmosphere, ○○○ CO atmosphere.

Experiments performed under an atmosphere of carbon monoxide did show, that the decomposition of $Co_2(CO)_8$ was second order in cobalt concentration. This can be seen from Figure 2, which also shows the effect of correcting for $Co_4(CO)_{12}$ decomposition.

The influence of carbon monoxide partial pressure was determined by measuring the initial rates of gas evolution under different CO–N_2 gas mixtures. The rate of gas evolution was strongly inhibited by carbon monoxide: constant values for the rate constant k were obtained if the rates measured at different carbon monoxide pressures were multiplied by the fourth power of p_{CO}. This can be seen from Table I.

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(1) P. Chini, *Inorg. Chim. Acta Reviews*, *2*, 31 (1968).
(2) L. Mond, H. Hirtz, and M. D. Cowap, *J. Chem. Soc.*, 798 (1910).
(3) R. Ercoli, P. Chini, and M. Massimauri, *Chim. e Ind.* (Milan), *41*, 132 (1959).
(4) R. Ercoli, F. Barbieri-Hermitte, and G. Natta, *Rend. Accad. Lincei Clas. Sci. Fis. Nat.*, *16*, 249 (1959).

Table I. Influence of p_{CO} on the rate of $Co_2(CO)_8$ decomposition Temperature 61°C Total pressure 0,97 atm.

p_{CO} [atm]	$k_{obs} \times 10^4$ [$l.mole^{-1} . sec^{-1}$]	$(p_{CO})^4$ [atm^4]	$(k = k_{obs}(p_{CO})^4) \times 10^6$ [$l.mole^{-1} . sec^{-1} . atm^4$]
0.78 [a]	1.75	0.372	6.51
0.59	5.36	0.121	6.48
0.39	28.4	0.023	6.53
0.22	260	0.0023	6.00

[a] This experiment was performed under carbon monoxide, the difference between total pressure and p_{CO} is due to toluene vapour pressure.

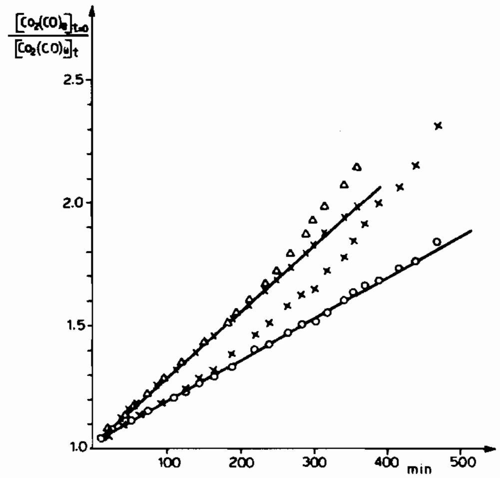

Figure 2. Decomposition of $Co_2(CO)_8$ in toluene solution, under carbon monoxide at 61°C; +, $[Co_2(CO)_8] = 0.115$ mmole/ml; ○, $[Co_2(CO)_8] = 0.115$ mmole/ml; after correction for $Co_4(CO)_{12}$ decomposition; △, $[Co_2(CO)_8] = 0.347$ mmole/ml; ×, $[Co_2(CO)_8] = 0.347$ mmole/ml; after correction for $Co_4(CO)_{12}$ decomposition.

The decomposition of $Co_2(CO)_8$ to $Co_4(CO)_{12}$ and CO can thus be represented by the following kinetic equation:

$$\frac{-d[Co_2(CO)_8]}{dt} = k[Co_2(CO)_8]^2(p_{CO})^{-4}$$

Based on this result, the following mechanism is suggested:

$$Co_2(CO)_8 \overset{K_1}{\rightleftharpoons} Co_2(CO)_7 + CO \qquad (1)$$

$$Co_2(CO)_7 \overset{K_2}{\rightleftharpoons} Co_2(CO)_6 + CO \qquad (2)$$

$$2Co_2(CO)_6 \xrightarrow[slow]{K_2} Co_4(CO)_{12} \qquad (3)$$

If the first two steps are regarded as rapid preequilibria, this mechanism leads to the rate equation

$$\frac{-[Co_2(CO)_8]}{dt} = K_1^2 . K_2^2 . k_2 . [Co_2(CO)_8]^2(p_{CO})^{-4}$$

which is in agreement with the experimental results if $k = K_1^2 . K_2^2 . k_2$.

Our experiments thus show that coordinatively unsaturated $Co_2(CO)_6$ fragments are necessary for the formation of the Co_4 cluster. This result and the mechanism found[5] for the reaction

$$2HCo(CO)_4 \longrightarrow Co_2(CO)_8 + H_2$$

(in which $HCo(CO)_3$ is formed in the first step) both stress the importance of coordinatively unsaturated intermediates in reactions leading to new cobalt-cobalt bonds.

Since the measured constant k is a product of equilibrium constants and the real rate constant k_2, a strong temperature dependence of the decomposition rate is to be expected. This was confirmed by experiments at diffrent temperatures, the results of which are compiled in Table II.

Table II. Effect of temperature on reaction rate

Temperature °C	k [$l.mole^{-1} . sec^{-1} . atm^4$]
40	2.1×10^{-7}
50	3.6×10^{-6}
61	6.5×10^{-5}

The apparent activation energy calculated from these data is 56 kcal/mole. This would be much too high for a simple chemical reaction in solution, but is quite acceptable as a sum of the following energy terms:

(i) twice the heats of reaction for both of step (1) and (2);

(ii) energy of activation for step (3).

The loss of one carbon monoxide ligand from simple cobalt carbonyls is accompanied by the absorption of roughly 10 kcal/mole: Ercoli and co-workers[4] calculated a value of 8.5 kcal/mole for $Co_2(CO)_8$, our measurements[5] furnished a value of 13 kcal/mole for $HCo(CO)_4$. This leaves for ΔH^* of step (3) somewhat around 15 kcal/mole, a not unreasonable value.

Finally it should be noted that, due to the $(p_{CO})^{-4}$ term in the rate equation, the stability of $Co_2(CO)_8$ solutions is very strongly dependent on carbon monoxide concentration. As to our experience, the formation of $Co_4(CO)_{12}$ in a N_2 atmosphere is significant already at room temperature, and accordingly, one

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(5) F. Ungváry and L. Markó, *J. Organometal. Chem.*, *20*, 205 (1969).

should use carbon monoxide as a protecting gas if working with $Co_2(CO)_8$.

Experimental Section

Experiments were performed in a thermostated reaction flask of glass, connected to a gas burette in which the gas was collected above toluene. The reaction was started by injecting through a silicone cap a known quantity of $Co_2(CO)_8$ dissolved in toluene into the reaction flask, containing already some toluene and previously heated to the desired temperature.

The influence of the glass surface on the reaction rate was controlled by experiments in the presence of glass powder.