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Redox Reactions of Metal Carbonyls. I. Kinetics and Mechanism of Disproportionation of $Co_2(CO)_8$ with Piperidine

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The disproportionation reaction of $Co_2(CO)_8$ by nucleophilic attack of piperidine has been investigated at different temperatures in n-heptane with the stopped-flow technique. The reaction is given by a series of successive and/or competitive pathways with different kinetic dependence on the ligand concentration. The experimental findings suggest that a rapid coordination of the ligand (L) occurs until the $Co_2(CO)_7L_3$ species is formed; then the adduct dissociates into ionic fragments. The mechanism and the kinetic parameters are discussed with reference to available findings on $Co_2(CO)_8$.

Introduction

Whenever a Lewis base attacks $Co_2(CO)_8$, either substitution and/or disproportionation can occur. With hard bases such those containing O or N donor atoms, disproportionation is favoured: that ultimately gives rise to Co(+II) and Co(–I) derivatives, according to the general stoichiometry shown in eq. (1) [1]:

$$3\ Co_2(CO)_8 + 12\ L \longrightarrow 2\ [CoL_6^{2+}] + 4\ [Co(CO)_4^-] + 8\ CO \qquad (1)$$

Soft bases, like phosphines, isocyanides *etc.* give a $Co^{+I}Co^{-I}$ salt, in which partial or complete carbonyl displacement of the cation takes place [2].

It is generally accepted that the first step of these reactions is the formation of the $[LCo(CO)_4^+]$ $[Co(CO)_4^-]$ salt. This assumption is essentially based on the experimental evidence of detection of the very unstable cobalt carbonyl cation with alcohols [3] or piperidine [4], to which the formula $[LCo(CO)_4^+]$ has been ascribed. Surprisingly, although these reactions are well known from many years, kinetic data are practically lacking. Only two non-detailed studies are reported, in which the dependence of the rates of the reactions between $Co_2(CO)_8$ and $P(C_6H_5)_3$ [5] or Cl^- [6] on the concentrations of both reactants is established. So we have begun a systematic study on the kinetics and mechanism of reaction (1). This paper reports the data concerning the reaction of $Co_2(CO)_8$ with piperidine.

Experimental

All the manipulations were carried out in a glovebox filled with dry nitrogen. Particular care was used to avoid any contact of the solvent or of the solutions of reactants with air.

$Co_2(CO)_8$ (Alfa Inorganics) was crystallised from n-heptane at –20 °C; piperidine (reagent grade) was distilled under reduced pressure on KOH pellets; n-heptane was distilled, dried on molecular sieves and swept with nitrogen.

The kinetic runs were carried out with a Durrum–Gibson stopped-flow spectrophotometer equipped with a thermostated cell with 2-cm optical path. The measurements were performed at 380 nm, where the molar absorptivity of $Co_2(CO)_8$ is about 2100 M^{-1} cm^{-1} and that of piperidine is negligible. Kinetic results were the same using different wavelengths in the range 350–450 nm. The reaction was studied under pseudo-first-order conditions with the concentration of the ligand much larger than that of the carbonyl complex. Values of the transmittance of the solution as a function of time were read from the photographs of the reaction traces on the oscilloscope screen. The pseudo-first-order rate constants, k_{obs}, were obtained from plots of $\ln(A_t - A_\infty)$ or $\ln(A_\infty - A_t)$ *vs.* time, where A_t and A_∞ are the absorbances at time t and at infinite time, respectively. When A_∞ has not been determined because of the subsequent steps of the reaction, k_{obs}

was calculated according to the Guggenheim method. Pseudo-first-order rate constants were reproducible to 10% or better.

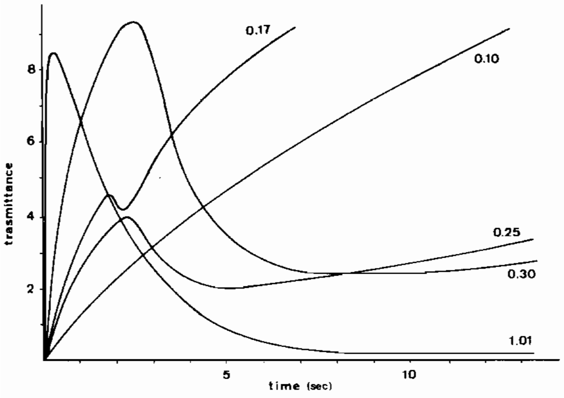


Figure 1. Traces of the reaction paths of $Co_2(CO)_8$ with piperidine at 24.8 °C. Plot of the transmittance *vs.* time (values indicate the ligand concentration).

Results and Discussion

Fig. 1 shows some typical traces of the paths of the reaction. Three different stages can clearly be identified. A first stage is characterised by an increase of the transmittance and its rate is strongly dependent on the concentration of piperidine. The second stage, which shows a large decrease of the transmittance, becomes evident at high concentration of the ligand; when a reliable measurement of the rate is obtained, it appears practically independent of [L]. The third stage seems more complicate and difficult to rationalize. The rate markedly decreases when the concentration of the ligand increases and becomes practically zero at high values of [L]. In some cases (not shown in Fig. 1) this stage shows a decrease of the transmittance. It is evident that two or more reactions are competitive, which probably show a different dependence on [L]: their identification is practically impossible.

The values of the observed rate constants of the first and the second stage for three different temperatures are reported in Table I: each value is the average of two or three different measurements.

The dependence of the pseudo-first-order rate constant of the first stage, $k_{obs}(I)$, on the concentration of piperidine shows a reaction order between 2 and 3, as easily ascertained by plotting $\ln k_{obs}(I)$ *vs.* $\ln[L]$. This value is practically constant at the different temperatures. Such behaviour can be rationalized in terms of the following mechanism:

$$Co_2(CO)_8 + L \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Co_2(CO)_8L$$

$$Co_2(CO)_8L + L \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Co_2(CO)_8L_2 \qquad (2)$$

$$Co_2(CO)_8L_2 + L \xrightarrow{k_3} Co_2(CO)_7L_3 + CO$$

If the intermediates $Co_2(CO)_8L$ and $Co_2(CO)_8L_2$ do not accumulate during the reaction, the steady-state approximation can be applied to them giving the following expression for the rate:

$$\text{rate} = k_{obs}(I)\,[Co_2(CO)_8] = \frac{k_1k_2k_3\,[Co_2(CO)_8]\,[L]^3}{k_{-1}k_{-2} + k_{-1}k_3\,[L] + k_2k_3\,[L]^2} \qquad (3)$$

The term $k_2k_3\ [L]^2$ is probably negligible with respect to $k_{-1}k_2 + k_{-1}k_3\ [L]$; so, on rearranging, eq. (4) can be obtained:

TABLE I. Pseudo-first-order Rate Constants for the Reaction of $Co_2(CO)_8$ with Piperidine in n-Heptane.

t, °C	Piperidine, *M*	$k_{obs}(I)$, sec^{-1}	$k_{obs}(II)$, sec^{-1}
10.5	0.10	0.049	
	0.13	0.103	
	0.17	0.251	
	0.25	0.92	
	0.30	1.08	
	0.40	4.2	
	0.50	7.0	0.22
	0.71	11.4	0.11
	0.75	16.4	0.13
	1.00	24.0	0.17
	1.51	110	0.14
	2.02		0.14
24.8	0.10	0.052	
	0.12	0.078	
	0.17	0.183	
	0.25	0.74	0.35
	0.26	0.79	
	0.29	0.76	
	0.40	3.1	
	0.50	3.5	0.30
	0.76	10.8	
	1.01	24.6	0.33
	1.51	68.0	0.29
	2.00	83	0.38
	3.00	350	0.33
38.6	0.12	0.093	
	0.13	0.102	
	0.17	0.182	
	0.30		1.4
	0.60	6.2	
	0.75	8.7	
	1.00	15.1	1.6
	1.51	46.5	1.4
	2.02	70.0	1.2

$$\frac{[L]^2}{k_{obs}(I)} = \frac{k_{-1}k_{-2}}{k_1k_2k_3} \cdot \frac{1}{[L]} + \frac{k_{-1}}{k_1k_2} \tag{4}$$

The linearity of the plots of $[L]^2/k_{obs}(I)$ *vs.* $1/[L]$, as shown in Fig. 2, supports the proposed mechanism. One should take into account the variation of the dielectric constant of the solvent medium, as the concentration of piperidine is, in some cases, very high. However the dielectric constant of piperidine (5.8) is not so different from that of n-heptane (1.9) to give rise to a gross change in the dielectric constant of the medium (the values vary between 1.9 and 3.1, from the less to the more concentrated solution). So the effect is probably negligible and could not change significantly the overall mechanism but could simply give rise to a small variation of the values of the slope and intercept.

A least-squares treatment of the experimental data according to eq. (4) gives the best values of the slope and intercept, from which the relevant activation parameters are calculated. All data are reported in Table II.

The rate of the second stage is practically independent of the concentration of piperidine, as shown by the values of $k_{obs}(II)$ (Table I). So the values of k(II), as the average of the observed rate constant, are reported in Table II, together with the relevant activation parameters.

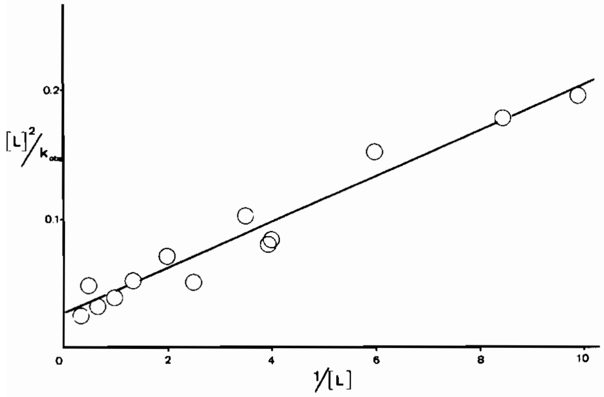
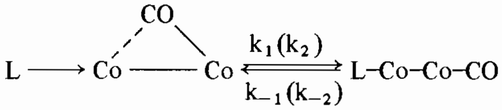


Figure 2. Plot of $[L]^2/k_{obs}(I)$ *vs.* $1/[L]$ (from eq. 4) at 24.8 °C.

Wender *et al.* reported [4] that the presumed initial intermediate in the reaction between $Co_2(CO)_8$ and piperidine is a thermally unstable salt of the type $[LCo(CO_4^+)]\,[Co(CO)_4^-]$. Experimental evidence was given for the final formation of the anion $[Co(CO)_4^-]$, but not of the cation, because of its rapid decomposition: so the structure of the intermediate remains speculative.

Our kinetic results indicate, as shown by eq. (2), three successive steps in the attack of piperidine on $Co_2(CO)_8$, each one giving the coordination of one molecule of ligand on the substrate. The first two steps are both reversible, the third one is not, because of the irreversible loss of a CO molecule. This could tentatively be explained assuming that each coordination of piperidine is accompanied by a concerted transfer of one CO from bridging to terminal position:



$$L \longrightarrow Co(\mu\text{-}CO)Co \underset{k_{-1}(k_{-2})}{\overset{k_1(k_2)}{\rightleftarrows}} L\text{–}Co\text{–}Co\text{–}CO \tag{5}$$

In such way both cobalt atoms retain the same coordination number they have in the starting carbonyl. Only the attack of the third molecule of ligand forces one CO group to leave the substrate. Therefore it should be remembered that $Co_2(CO)_8$ exists in solution as an equilibrium mixture of bridged and nonbridged isomers [7], whose equilibrium constant is about unity at room temperature in hydrocarbon solution [8]. So we must take into account the possibility that the ligand coordinates on the nonbridged form. In this case the coordination could be accompanied by a transfer of one CO from terminal to bridging position, so the intermediate of the attack of the first molecule of piperidine is the same, whatever is the reactive isomer. Kinetically, the equilibrium between the two forms is without effect on the reaction mechanism, if it is established very rapidly. This appears to be the case, as the value of the rate of interconversion, though unknown, is probably very high if compared to the rate of reaction (1) [9].

It is not evident if the ligand coordinates to the same cobalt atom or, symmetrically, to both atoms,

TABLE II. Specific Rate Constants and Activation Parameters for the Reaction of $Co_2(CO)_8$ with Piperidine in n-Heptane.

t, °C	Slope[a,b], 10^2 sec M^3	Intercept[a,c], 10^2 sec M^2	k(II)[d], sec^{-1}
10.5	1.93 ± 0.13	0.8 ± 0.6	0.15 ± 0.01
24.8	1.77 ± 0.13	2.7 ± 0.6	0.33 ± 0.02
38.6	1.47 ± 0.20	4.6 ± 0.9	1.4 ± 0.1

[a] From eq. (4). [b] $\Delta H^* = -1.1 \pm 0.8$ Kcal/mol; $\Delta S^* = -74 \pm 3$ e.u. [c] $\Delta H^* = 10.5 \pm 4.0$ Kcal/mol; $\Delta S^* = -31 \pm 13$ e.u. [d] $\Delta H^* = 13 \pm 5$ Kcal/mol; $\Delta S^* = -15 \pm 16$ e.u.

giving *e.g.* $Co(CO)_3L_2{-}Co(CO)_5$ (a) or $[Co(CO)_4L]_2$ (b). (a) seems more likely because the attack of the first ligand on the metal could polarise the Co–Co bond in the sense $L \rightarrow Co^+ \rightarrow Co^-$ and so favour the second attack on the same atom. This suggestion is supported by the isolation of ionic compounds such as $[Co(CO)_3(PR_3)_2^+]$ $[Co(CO)_4^-]$ from the reaction of dicobaltoctacarbonyl and trialkyl- or triarylphosphines [2, 12].

The values of the activation parameters are scarcely significant, indicating only the complexity of the reaction mechanism. However, it should be pointed out that the slope/intercept ratio gives the values k_{-2}/k_3, from which it is easily obtained that ΔH_3^* is about 12 Kcal/mol greater than ΔH_{-2}^*. As k_3 is referred to a process implying a Co–L bond forming together with a Co–Co bond breaking (so ΔH_3^* cannot be greatly positive), ΔH_{-2}^* must be near zero. This is possible if in the k_{-2} process the release of L is accompanied by an internal rearrangement, similar to that indicated by the reversal of eq. (4).

The second stage, whose rate is independent of [L], can be explained as an internal dissociation of the final product of the first stage. A possible interpretation, which could be regarded as tentative is given by eq. 5:

$$Co(CO)_2L_3{-}Co(CO)_5 \xrightarrow{k(II)} [Co(CO)_2L_3^+][Co(CO)_4^-] + CO \quad (5)$$

i.e., increasing polarization of the metal–metal bond during ligand attack gives rise to a complete ionic dissociation, together with a loss of CO from the anionic fragment to give the stable $Co(CO)_4^-$ ion. Both ions are probably solvated to the same extent by the excess of piperidine, in agreement with the observation that $Co(CO)_4^-$ strongly interacts with polar solvent molecules such as piperidine, tetrahydrofuran *etc.* [13]. That accounts for the large variation of absorbance associated to this stage and for its increasing appearance when the concentration of the ligand increases (see Fig. 1). The value of ΔH_{II}^* is plausible as the enthalpy variation for the Co–Co and Co–CO bond breaking is probably higher than for the ion–solvent bond making. The negative value of ΔS_{II}^* is also acceptable, as it indicates a decrease of degrees of freedom during the reaction, due to the quite strong interaction of the ions with piperidine.

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