

Mechanistic studies on the disproportionation of dicobalt octacarbonyl with hard Lewis bases *

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Abstract

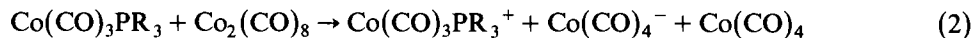
The disproportionation of $\text{Co}_2(\text{CO})_8$ by pyridine has been found to be inhibited by CO. The reaction orders in respect of $\text{Co}_2(\text{CO})_8$ and pyridine are fractional, and depend on the partial CO pressure. A radical mechanism with partial chain character is proposed. The reaction appears to involve inner sphere electron transfer processes.

Introduction

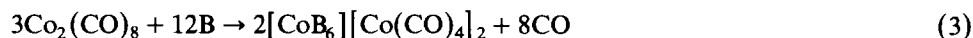
The disproportionation of dicobalt octacarbonyl in the presence of Lewis bases was first observed three decades ago [1], but the mechanistic features of these complex reactions are still not really understood. With soft bases (e.g. with phosphines) $[\text{Co}^+, \text{Co}(\text{CO})_4^-]$ ion pairs are formed:



It was proved that in these cases disproportionation is a radical chain reaction [2]. An outer sphere electron transfer was proposed for another step of the reaction:



With hard Lewis bases $\text{Co}_2(\text{CO})_8$ reacts to form ion pairs, $[\text{Co}^{2+}, 2 \text{Co}(\text{CO})_4^-]$



* Dedicated to Professor Luigi Sacconi in recognition of his important contributions to organometallic chemistry.

Kinetic studies of reaction 3 in the case of various amines did not provide a clear mechanistic interpretation [3]. On the basis of an analogy with the photoinduced disproportionation of $\text{Mn}_2(\text{CO})_{10}$, a radical chain mechanism was also postulated for reaction 3 [4]. A similar proposal was based on an infrared spectroscopic study of the $\text{Co}^{2+}/\text{pyridine}/\text{Co}(\text{CO})_4^-$ system in THF [5].

The $\text{Co}_2(\text{CO})_8/\text{pyridine}$ systems are known to activate small molecules such as H_2 , HSiR_3 , and ROH [5,6], and consequently they are of importance in homogeneous catalysis [7]. Increase of knowledge of reaction 3 ($\text{B} = \text{Py}$), could lead to a better understanding of these catalytic processes and the present paper presents the results of a kinetic study of the reaction between $\text{Co}_2(\text{CO})_8$ and pyridine.

Experimental

Materials. Toluene and pyridine were purchased from Reanal (Hungary). Toluene was dried over sodium wire and pyridine over KOH pellets, and both were distilled and stored under CO. Dicobalt octacarbonyl was prepared by the usual method [8], and recrystallized from CH_2Cl_2 and then from heptane.

Kinetic techniques. Infrared spectra were recorded on Carl Zeiss Jena UR 20 and IR 75 spectrophotometers. In all cases the $\log I_0/I$ values of the 2070 cm^{-1} band ($\epsilon_M 3810 \pm 60\text{ M}^{-1}\text{ cm}^{-1}$, in toluene) were determined.

Reactions at atmospheric pressure were run in a thermostatted vessel at 25°C under CO. They were initiated by injecting a $\text{Co}_2(\text{CO})_8$ stock solution into a vigorously stirred toluene solution of an excess of pyridine. The reaction was monitored by taking samples with a gas-tight syringe and transferring them with the aid of a three-way valve and Teflon tubing into a thermostatted IR cell (0.0528 and 0.0232 cm, CaF_2). The initial rates were calculated from plots up to 10% conversion, and were reproducible within $\pm 5\%$.

At higher CO pressures a stainless steel microreactor-cell system was used [9]. The reactor (3 ml) was connected directly to the cell (0.098 cm, NaCl) and equipped with a calibrated Bourdon-type manometer having an accuracy of $\pm 2.5\%$. Stirring was performed by a micro cog-wheel pump built into the cell-body. The toluene and the $\text{Co}_2(\text{CO})_8$ stock solution were placed in the reactor under CO. The reactor was then closed and connected to a six-way stainless steel microvalve. The reactor was pressurized and stirred for 15 minutes to ensure equilibrium of the two phases. The required amount of the pyridine stock solution was injected into the bore of the stainless steel valve and the reaction was started by turning the valve and using toluene as the flushing solvent. The pressure of CO in the reactor increased by less than 0.5 bar during this injection. The absorbance at 2070 cm^{-1} was measured continuously, and the initial rates were reproducible within $\pm 10\%$.

Results

The initial rates of disproportionation of $\text{Co}_2(\text{CO})_8$ at 25°C in the presence of pyridine are listed in Table 1. Figure 1 shows plots of the rate against the concentration of $\text{Co}_2(\text{CO})_8$ or pyridine.

The initial rate decreased with increasing CO pressure, and the order with respect to CO was found to be about minus one. At 12 bar CO pressure the order for

$\text{Co}_2(\text{CO})_8$ was somewhat higher than one and for pyridine less than one. At atmospheric pressure both orders were considerably smaller (see Fig. 1). Galvinoxyl (1% based on $\text{Co}_2(\text{CO})_8$) reduced the rate by a factor of 1.5.

Immediately after the reaction was initiated a weak shoulder around 2080 cm^{-1} appeared in the $\nu(\text{CO})$ spectrum, and at the same time the bands in the regions $2050\text{--}1990$ and $1870\text{--}1820\text{ cm}^{-1}$ became somewhat more intense and broadened. The ratios of the heights of original $\text{Co}_2(\text{CO})_8$ bands to those of the new bands remained unchanged during the reaction. When a 0.1 M $\text{Co}_2(\text{CO})_8$ solution in toluene was treated with an equimolar amount of pyridine at 25°C for 5 min, then frozen at 78°C to remove unchanged $\text{Co}_2(\text{CO})_8$, some $\text{Co}_4(\text{CO})_{12}$, $\text{Co}_3(\text{CO})_{10}^-$ (presumably with Co^{2+} as counterion), and a new species A were detected by IR

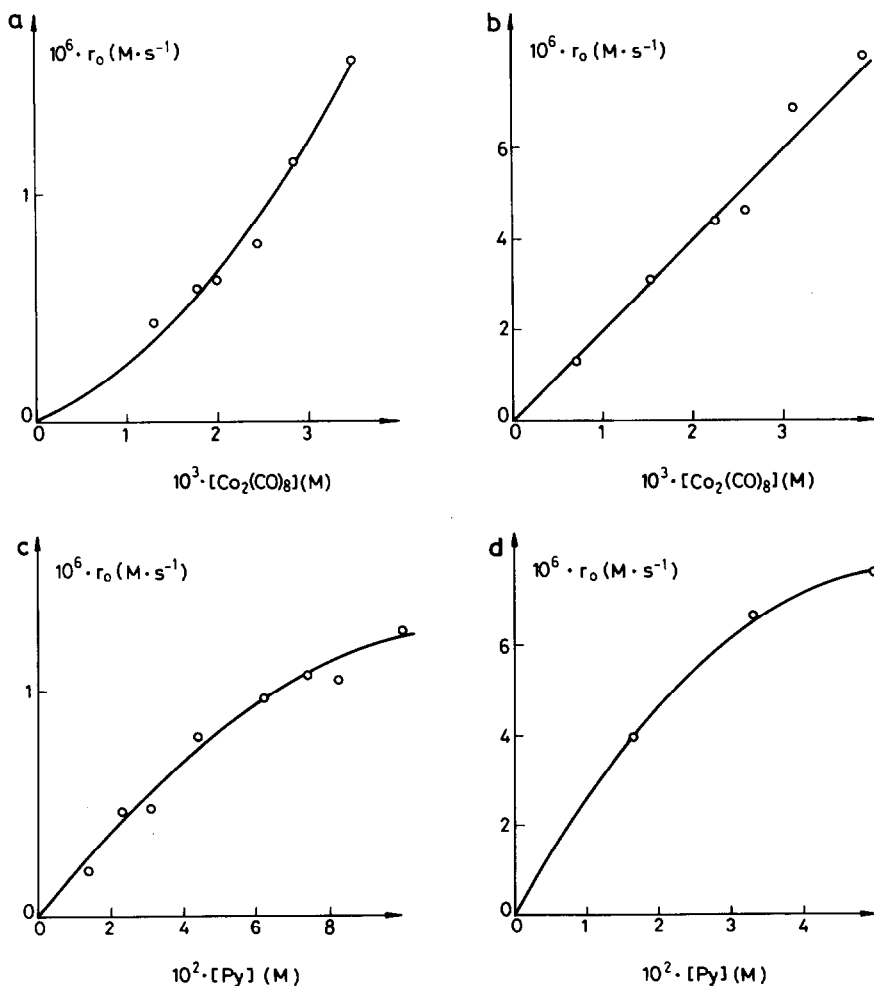


Fig. 1. Plots of initial rates of the disproportionation of $\text{Co}_2(\text{CO})_8$ in the presence of pyridine in toluene at 25°C against (a) $\text{Co}_2(\text{CO})_8$, at $[\text{Py}] 6.3 \times 10^{-2}\text{ M}$ and $p_{(\text{CO})} 12\text{ bar}$; (b) $\text{Co}_2(\text{CO})_8$, at $[\text{Py}] 3.3 \times 10^{-2}\text{ M}$ and $p_{(\text{CO})} 0.93\text{ bar}$; (c) $[\text{Py}]$, at $[\text{Co}_2(\text{CO})_8] 2.6 \times 10^{-3}\text{ M}$ and $p_{(\text{CO})} 12\text{ bar}$; (d) $[\text{Py}]$, at $[\text{Co}_2(\text{CO})_8] 3.0 \times 10^{-3}\text{ M}$ and $p_{(\text{CO})} 0.93\text{ bar}$.

Table 1

Kinetic data for the disproportionation of dicobalt octacarbonyl in the presence of pyridine in toluene ^a

$10^3 [\text{Co}_2(\text{CO})_8]$ (<i>M</i>)	$10^2 [\text{Py}]$ (<i>M</i>)	$p(\text{CO})$ (bar)	$10^7 r_0$ (<i>M s</i> ⁻¹)
0.74	3.35	0.93	13.7
1.54	3.35	0.93	31.4
2.27	3.33	0.93	44.2
2.61	3.33	0.93	46.4
3.13	3.31	0.93	69.6
3.93	3.30	0.93	81.0
3.01	1.68	0.93	39.8
2.97	4.91	0.93	75.8
2.54 ^b	3.33	0.93	28.0
1.28	6.28	12.7	4.2
1.75	6.35	12.0	6.0
2.00	6.38	12.0	6.2
2.45	6.30	11.8	8.9
2.85	6.27	11.8	11.5
3.50	6.40	11.9	16.0
2.60	1.37	11.7	1.9
2.55	2.30	12.0	4.7
2.56	3.18	11.8	4.8
2.57	4.39	11.6	8.1
2.85	7.42	11.7	12.6
2.54	8.33	12.0	10.4
2.70	10.10	12.7	12.1
2.42	6.32	6.8	14.7
2.64	6.85	15.4	6.7
2.63	6.83	19.9	5.6

^a Atmospheric runs: 25.0 °C; Pressurized runs 25 ± 1 °C. ^b Galvinoxyl (1% based on $\text{Co}_2(\text{CO})_8$) was added.

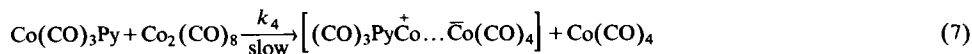
spectroscopy. A gave bands at 2081 m, 2035s, and 1827m cm^{-1} (some other bands may have been obscured). Unfortunately, attempts to isolate A failed.

Discussion

The kinetic data obtained suggest a complicated reaction pathway with some radical chain character. In spite of similarities to the features described [2] for reaction 1, there are the following significant differences:

- (i) The disproportionation in the presence of pyridine is slower by about two orders of magnitude than that in the presence (sterically not hindered) phosphines under similar conditions.
- (ii) Reaction 3 ($\text{B} = \text{Py}$) is inhibited by CO. No such effect was reported in the case of phosphines.
- (iii) Homonuclear ion pairing (HNIP, cf. refs. 2 and 5) was found for $[\text{CoPy}_6][\text{Co}(\text{CO})_4]_2$ (and intermediates), whereas $[\text{Co}(\text{CO})_3(\text{PR}_3)_2][\text{Co}(\text{CO})_4]$ complexes exist as discrete ions in solutions.

These features suggest the radical intermediate, $\text{Co}(\text{CO})_3\text{Py}$, is probably formed through a dissociative than an associative route (see also below). Reversible recom-



Scheme 1. Proposed mechanism of the disproportionation of $\text{Co}_2(\text{CO})_8$ with pyridine.

bination of this species with $\text{Co}(\text{CO})_4$ could lead to $\text{Co}_2(\text{CO})_7\text{Py}$, which may be A in view of the IR data for the latter (cf. ref. 5). The large rate differences between the reactions with phosphines and those with pyridine and the probable formation of HNIP intermediates in the latter case suggest that the first electron transfer is an inner sphere process. A reasonable reaction pathway is shown in Scheme 1.

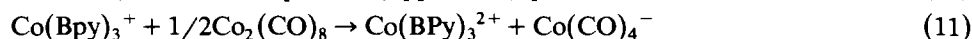
The rate law derived [10] from this scheme (the presumably fast equilibrium 8 being neglected) is in accord with the experimental results:

$$r = -\frac{d[\text{Co}_2(\text{CO})_8]}{dt} = \frac{(k_1/k_{-1})^{1/2} k_2 k_3 k_4 [\text{Co}_2(\text{CO})_8]^{3/2} [\text{Py}]}{k_3 k_4 [\text{Co}_2(\text{CO})_8] [\text{Py}] + k_{-2} (k_{-3} + k_4 [\text{Co}_2(\text{CO})_8]) [\text{CO}]}$$

Using experimental [11] or estimated [2] k values for reactions 4-6, k_4 was calculated to be about 10^4 , a reasonable value. Since the concentration of the active species $\text{Co}(\text{CO})_3\text{Py}$ cannot be higher than $10^{-9} M$ under the conditions used, the first electron transfer step (eq. 7) becomes rate determining. Thus the relatively weak chain character of the process (cf. the moderate effect of galvinoxyl) can be accounted for.

The second electron transfer in reaction 3 also presumably takes place through HNIP species (cf. ref. 5), and so it too must be an inner sphere process.

Although the results obtained by Fachinetti and his coworkers [5,12] support the role of HNIP species in reaction 3 for most hard bases, our experiments show that in special cases, e.g. for chelating bases, mononuclear intermediates seem to be more likely. Thus we found that the rate of $\text{Co}_2(\text{CO})_8$ disproportionation in the presence of 2,2'-bipyridine (Bpy) (eq. 10) is much higher than that in the presence of pyridine; so high, in fact, that the rates could not be measured by our IR methods. However, the Co^+ complex $[\text{Co}(\text{Bpy})_3][\text{ClO}_4]$ could be prepared by an independent method [13], and thus we were able to model the assumed last step of reaction 10 (eq. 11) *:



This reaction, which is accompanied by the disappearance of the deep blue color of the Co^+ species, was practically instantaneous. Since both reactants have filled

* The products of reaction 11 were identified on the basis of their IR and UV-VIS spectra, respectively.

coordination spheres, an outer sphere electron transfer seems to be more probable in this case.

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