THE EFFECT OF $Co_2(CO)_8$ ON THE DECOMPOSITION OF $CoH(CO)_4$

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Summary

The thermal decomposition of $CoH(CO)_4$ in solution to $Co_2(CO)_8$ and H_2 is catalyzed by $Co_2(CO)_8$; the effect of the latter is proportional to the square root of the concentration. Probably the $Co(CO)_4\cdot$ radical is involved in the process. One-electron reactions of the trityl radical with $CoH(CO)_4$ and benzophenone ketyl with $Co_2(CO)_8$ are described.

Introduction

The rate of the thermal decomposition of $CoH(CO)_4$ in solution to give Co_2-$(CO)_8$ and H_2 was previously found to be second order with respect to CoH-$(CO)_4$ and inversely proportional to the concentration of CO [1,2]. In addition Orchin and coworkers found that the presence of as little as 0.1 equivalent of $Co_2(CO)_8$ per $CoH(CO)_4$ reduced the "induction period" of the reaction and caused a slight rate increase [2]. Later we observed that the rate of hydrogenation of diethyl fumarate by $CoH(CO)_4$ was significantly increased by $Co_2(CO)_8$ [3]. The effect of $Co_2(CO)_8$ on the reactivity of $CoH(CO)_4$ thus seemed to be a more general one, and so to merit further investigation.

Results and discussion

We confirmed the observation of Orchin and coworkers [2] that the rate of $CoH(CO)_4$ decomposition in solution increases with the degree of conversion. The amount of H_2 evolved as a function of time in two separate experiments is shown in Fig. 1 and the curves are obviously similar to those which are regarded as characteristic of autocatalytic reactions. This observation alone cannot, however, be regarded as a proof for some catalytic effect of $Co_2(CO)_8$ on the decomposition of $CoH(CO)_4$, since the rate increase may also be caused by the H_2 evolved in the reaction, which dilutes the gas phase above the reaction mixture and thus decreases the concentration of CO.
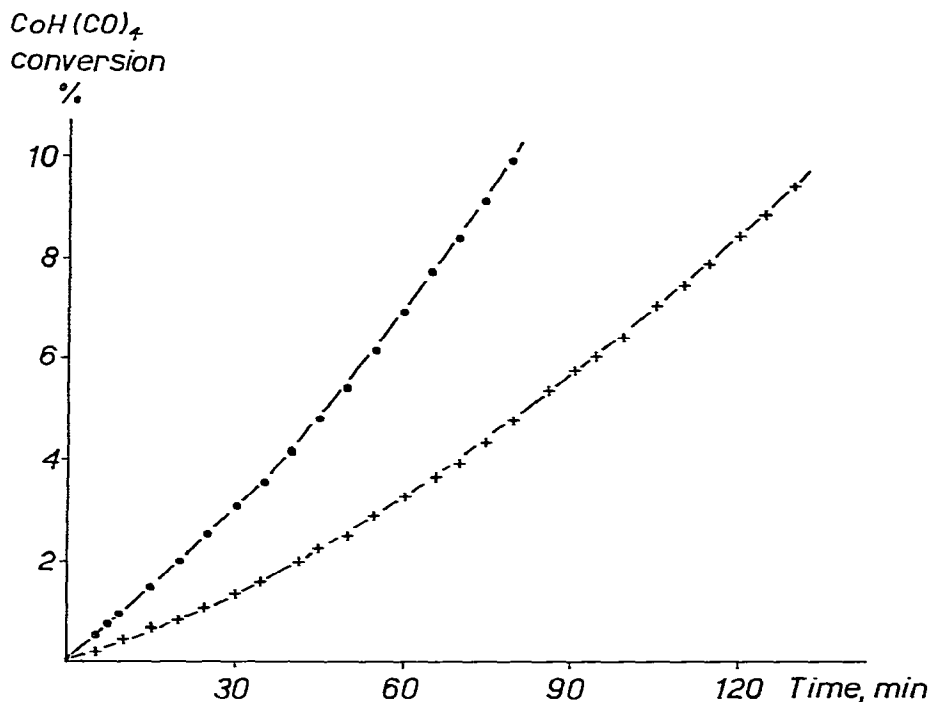
Fig. 1. Decomposition of CoH(CO)$_4$ to Co$_2$(CO)$_8$, showing the acceleration of the rate during a run. Heptane solution, 30°C, no Co$_2$(CO)$_8$ added. Conversions calculated from the volume of H$_2$ evolved. · — · — · [CoH(CO)$_4$]$_0$ = 0.191 mol l^{-1} ; [CO]$_0$ = 0.0106 mol l^{-1} ; —+—+— [CoH(CO)$_4$]$_0$ = 0.361 mol l^{-1} ; [CO]$_0$ = 0.0105 mol l^{-1}.

If the decomposition of CoH(CO)$_4$ is actually catalyzed by Co$_2$(CO)$_8$ the rate equation determined for this reaction [1] may be wrong in several respects, since it is obviously practically impossible to prepare solutions of CoH(CO)$_4$ totally free of Co$_2$(CO)$_8$, and so any variation in the initial concentration of CoH(CO)$_4$ also changes the concentration of Co$_2$(CO)$_8$. We thus decided to carry out kinetic experiments on the decomposition of CoH(CO)$_4$ in heptane, and to work in the presence of known and relatively large amounts of deliberately added Co$_2$(CO)$_8$ to avoid any error caused by the small and varying Co$_2$-(CO)$_8$ content of the CoH(CO)$_4$ solutions. The results of our experiments are summarized in Table 1.

Based on these results the following conclusions seem to be justified:

a) Co$_2$(CO)$_8$ catalyzes the reaction;

b) wrapping the reaction flask in aluminium foil does not change the rate, which shows that the diffuse light of the laboratory has no effect on the reaction;

c) the approximate empirical rate equation is:

$$-\frac{d[CoH(CO)_4]}{dt} = k_{obs} \frac{[Co_2(CO)_8]^{0.5}[CoH(CO)_4]^2}{[CO]^2}$$

This is different from that found earlier [1] in the absence of relatively large

TABLE 1

INITIAL RATES (r) OF CoH(CO)$_4$ DECOMPOSITION IN HEPTANE SOLUTION UNDER CO AT VARIOUS INITIAL CONCENTRATIONS AND TEMPERATURES. TOTAL PRESSURE: 741 ± 3 mmHg

Temp.[a] (°C)	[CoH(CO)$_4$] (mol l^{-1})	[CO][b] × 10^2 (mol l^{-1})	[Co$_2$(CO)$_8$] (mol l^{-1})	r × 10^4 (mol l^{-1} min^{-1})
20	0.261	1.05	0.0473	1.5
20	0.265	1.05	0.234	3.4
30	0.069	1.07	0.108	0.40
30	0.140	1.07	0.108	2.3
30	0.142	1.07	0.108	2.4[c]
30	0.206	1.06	0.108	5.7
30	0.302	1.06	0.108	12.7
30	0.164	1.07	0.145	4.1
30	0.164	2.27[d]	0.145	0.86
30	0.164	2.30[e]	0.145	1.0
30	0.164	3.47[f]	0.145	0.32
40	0.090	1.07	0.0331	3.3
40	0.090	1.07	0.0940	5.6
40	0.090	1.07	0.292	9.7

[a] ±0.1°C; [b] calculated from p_{CO} using solubility data [4]; [c] experiment in the dark (cf. text); [d] under 1500 mmHg total pressure; [e] under 1520 mmHg total pressure; [f] under 2261 mmHg total pressure.

amounts of Co$_2$(CO)$_8$. Such a complex relationship obviously points to a rather complicated reaction mechanism.

We are unable at present to interpret in detail the above rate equation, and wish to comment only on the catalytic effect of Co$_2$(CO)$_8$.

The exponent 0.5 which applies to the Co$_2$(CO)$_8$ concentration suggests that a mononuclear species present in small quantities in equilibrium with Co$_2$-(CO)$_8$ is responsible for the catalysis, and the most likely species is the Co(CO)$_4$ radical. This radical has repeatedly been observed by spectroscopic methods [5], and recently the proposal has been made that this radical may play a role in the homogeneous hydrogenation of aromatic hydrocarbons [6] or carbon monoxide [7] in the presence of Co$_2$(CO)$_8$. In these latter reactions Co(CO)$_4$· is thought to be formed through the homolytic fission of the Co—H bond.
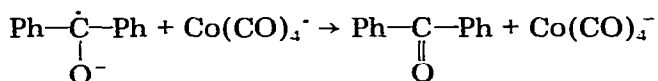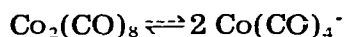
The accumulated evidence accordingly suggests that one-electron transfer processes should be also taken into account in interpreting the chemistry of cobalt carbonyls. To support this view we report below on two further examples of such one-electron reactions of cobalt carbonyls recently observed by us.

(1) CoH(CO)$_4$ reacts with the trityl radical in a fast and quantitative reaction to form triphenylmethane and Co$_2$(CO)$_8$. A reasonable mechanism for this reaction may be the following:

$$Ph_3C· + CoH(CO)_4 \xrightarrow{benzene} Ph_3CH + Co(CO)_4·$$

$$2 Co(CO)_4· \rightleftharpoons Co_2(CO)_8$$
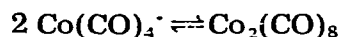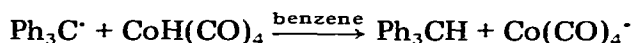
(2) The dark blue solution of ketyl radicals obtained from benzophenone and sodium in ether instantaneously becomes colourless upon addition of Co$_2$(CO)$_8$ and Co(CO)$_4^-$ is formed. The following mechanism is proposed for

this reaction:

$$Co_2(CO)_8 \rightleftharpoons 2\,Co(CO)_4^{\cdot}$$

$$Ph-\overset{\cdot}{\underset{O^-}{C}}-Ph + Co(CO)_4^{\cdot} \rightarrow Ph-\overset{\parallel}{\underset{O}{C}}-Ph + Co(CO)_4^-$$

Summarizing, in addition to coordinatively unsaturated intermediates, the role of which has been already recognized, radical species also probably play a significant role in the thermal decomposition of $CoH(CO)_4$ to $Co_2(CO)_8$. This seemingly simple reaction is apparently a rather complex process and even the possibility that the reaction has several parallel mechanisms must be considered. Similar considerations may apply to much of the industrially important catalytic chemistry of cobalt carbonyls.

Finally, it should be noted that $Co_4(CO)_{12}$ had no effect on the decomposition of $CoH(CO)_4$ under our conditions.

Experimental

Decomposition of $CoH(CO)_4$, kinetic measurements

Oxygen-free heptane saturated with CO was used for preparing stock solutions of $CoH(CO)_4$ and $Co_2(CO)_8$. Experiments were carried out in a thermostatted flask equipped with a reflux condenser and connected to a gas burette. The reflux condenser and the gas burette were thermostatted at $12°C$. Effective stirring was maintained by use of a magnetic stirring rod. The desired pressure of CO in the reaction flask and in the gas burette was maintained by using a thermostatted 2 l buffer flask. The pressure was checked with a mercury column. Heptane and the $Co_2(CO)_8$ solution were added from a syringe through a silicone rubber cap. When vapour—liquid equilibrium was reached, the reaction was started by introducing the $CoH(CO)_4$ solution in the same way. The decomposition was followed gasometrically by measuring the volume of hydrogen evolved.

Reaction of the triphenylmethyl radical with $CoH(CO)_4$

Solutions of triphenylmethyl radical were prepared in oxygen free absolute benzene under argon as follows. A solution of 6 g Ph_3CCl in 50 ml benzene was stirred with 15 g zinc powder fow 30 minutes at reflux temperature. The slurry was filtered and washed with 5 ml benzene. The resulting deep yellow solution was stirred at reflux temperature once again with an additional portion of 15 g zinc powder to react with remaining traces of the Ph_3CCl. The slurry was filtered and washed with 5 ml benzene. The resulting solution was chlorine free and contained 0.36 mmol/ml "triphenylmethyl", as confirmed by evaporation.

By mixing 1.6 mmol $CoH(CO)_4$ in 2 ml heptane with 1.58 mmol triphenylmethyl in 4.4 ml benzene solution under CO at $2°C$ a dark brown solution resulted within a minute without any gas evolution. The IR spectrum showed $Co_2(CO)_8$ to be the only cobalt carbonyl present. Upon adding 0.26 ml (3.3 mmol) DMF to the brown solution at room temperature, CO was evolved and a

clear solution resulted, together with a pink coloured crystalline salt which was removed by filtration. Evaporation of the solvent from the filtrate gave 0.36 g of triphenylmethane (mp = 92°C; 93% yield), which gave 0.33 g as colourless needles after recrystallization from 3 ml pentane (mp 94°C; 84% yield).

The reaction of $Co_2(CO)_8$ with benzophenone ketyl

A dark blue benzophenone ketyl solution was prepared from 1 g benzophenone, 500 ml absolute diethyl ether and ca. 2 g sodium wire by refluxing the mixture for several hours. 50 ml of this solution was transferred to a Schlenk tube under argon and 100 mg crystalline $Co_2(CO)_8$ was added. The solution almost immediately became colourless. The IR spectrum of the solution showed [Co-$(CO)_4$]$^-$ to be the only cobalt carbonyl present.

References

1 F. Ungváry and L. Markó, J. Organometal. Chem., 20 (1969) 205.
2 J.F. Terapane, Jr., Ph.D. Thesis, University of Cincinnati, Cincinnati, Ohio, 1969; A.C. Clark, J.F. Terapane, Jr. and M. Orchin, J. Org. Chem., 39 (1974) 2405.
3 J. Csizmadia, F. Ungváry and L. Markó, Trans. Metal. Chem., 1 (1976) 170.
4 F. Ungváry, J. Organometal. Chem., 36 (1972) 363.
5 H.J. Keller and H. Wawersik, Z. Naturforsch. B, 20 (1965) 938; D.R. Bidinosti and N.S. McIntyre, Chem. Commun., (1967) 1, D.R. Bidinosti and N.S. McIntyre, Can. J. Chem., 48 (1970) 593; O. Crichton, M. Poliakoff, A.J. Rest and J.J. Turner, J. Chem. Soc., Dalton Trans., (1973) 1321; L.A. Hanlan, H. Huber, E.P. Kündig, B.R. McGarvey and G.A. Ozin, J. Amer. Chem. Soc., 97 (1975) 7054; G. Bor, K. Dietler and K. Noack, J. Chem. Soc. Chem. Commun., (1976) 914; R.L. Sweany and T.L. Brown, Inorg. Chem., 16 (1977) 421; P. Wermer, B.S. Ault and M. Orchin, J. Organometal. Chem., 162 (1978) 189.
6 H.M. Feder and J. Halpern, J. Amer. Chem. Soc., 97 (1975) 7186.
7 J.W. Rathke and H.M. Feder, J. Amer. Chem. Soc., 100 (1978) 3623.