Preliminary communication

EVIDENCE FOR A RADICAL CHAIN PATHWAY FOR SUBSTITUTION OF $Co_2(CO)_8$

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Summary

The reaction between octacarbonyldicobalt, $Co_2(CO)_8$, and tri-n-butylphosphine at 25°C to yield $[Co(CO)_3(PR_3)_2]Co(CO)_4$ has been studied using IR stopped-flow techniques. The reaction is very rapid; the half-life at 25°C is on the order of 0.07 sec. The observations are consistent with a radical chain mechanism that includes an outer-sphere electron transfer from $Co(CO)_3L^{.}$ radical to $Co_2(CO)_8$.

Despite the immense importance of octacarbonyldicobalt $Co_2(CO)_8$, in organometallic chemistry [1, 2], the mechanisms of its substitution reactions are not understood. The scattered observations of substitution [3—16] and exchange reactions [17], and reactions with acetylenes [18], point to an exceptional range in characteristic rates, depending on the attacking moiety. We report here quantitative kinetic data for a rapid substitution process at room temperature that provide strong evidence for a radical chain mechanism.

Reaction of $Co_2(CO)_8$ with certain phosphines and phospites proceeds as in eq. 1.

$$Co_2(CO)_8 + 2L \rightarrow [Co(CO)_3L_2][Co(CO)_4] + CO \qquad (1)$$

The reaction when L is triphenylphosphine has been reported as very fast [15]; a rate constant was not obtainable at 0°C, but a pseudo first-order rate constant on the order of 5×10^{-4} sec^{-1} was observed at −72°C. We have observed the reaction between $Co_2(CO)_8$ and tri-n-butylphosphine, P(n-Bu)$_3$, in hexane solution at 25°C, using a stopped-flow apparatus with provision for maintaining an inert atmosphere, and with capability for observation of absorbance changes in the IR [19]. The reaction could be followed by observing the disappearance of the $Co_2(CO)_8$ absorption at 2043 cm^{-1}, or by observing the appearance of the absorption band due to the product salt, $\{Co(CO)_3[P(n-Bu)_3]_2\}\{Co(CO)_4\}$, at 1995 cm^{-1}.
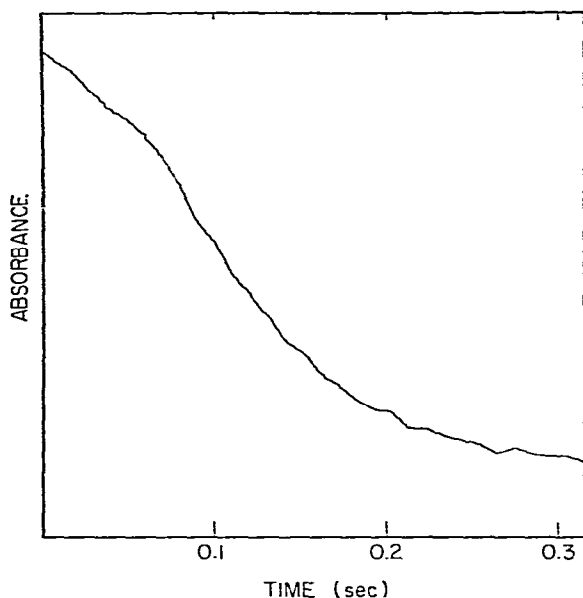
Figure 1 shows a typical absorbance vs. time plot for disappearance of

Fig. 1. IR absorbance due to $Co_2(CO)_8$ at 2043 cm^{-1} vs. time upon reaction with tri-n-butylphosphine at 25°C. Initial concentrations are $[Co_2(CO)_8]$ 1.52 × 10^{-3} M, $[P(n\text{-}Bu)_3]$ = 3.0 × 10^{-2} M.

$Co_2(CO)_8$. The reaction is very fast; under such typical initial concentration conditions, the first half-life is in the range from 0.07 to 0.10 sec. An induction period, evident in Fig. 1, is observed in all kinetic runs with $P(n\text{-}Bu)_3$ as ligand in both the appearance of product and disappearance of $Co_2(CO)_8$. Among other important observations are the following: the rate data for the first 4 to 6 half-lives in each reaction, run under conditions of excess ligand, exhibit good first-order rate plots following the initial induction period. The variation in these pseudo first-order rate constants as a function of initial ligand concentration in the range 3.0 × 10^{-2} to 9.0 × 10^{-2} M, is shown in Fig. 2 for hexane or CH_2Cl_2 as solvents. The rates are very similar in the two solvents, but the order in ligand may be somewhat different; least squares fits yield an order of 0.6 in hexane, 0.4 in CH_2Cl_2. The reaction rate is very markedly reduced throughout the course of reaction by addition of low concentrations of dioxygen.
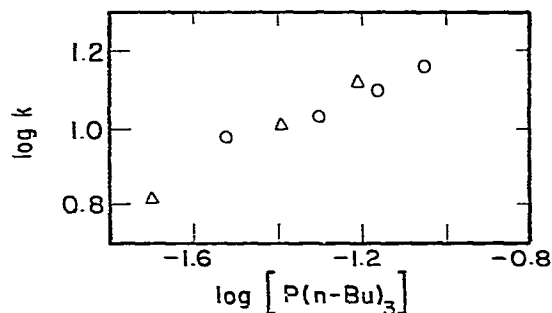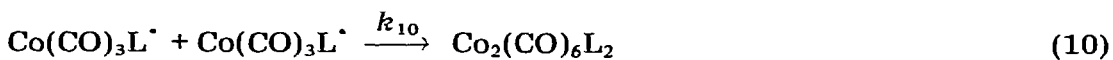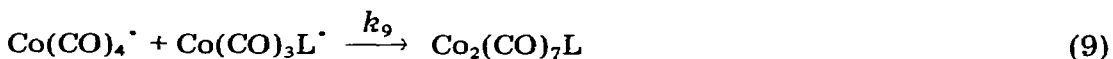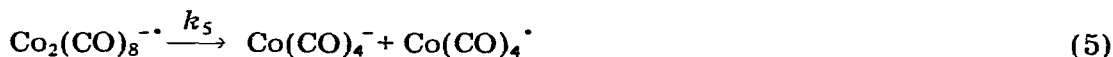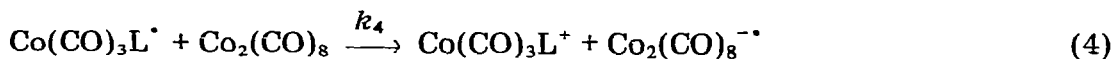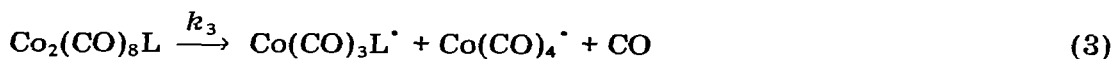

Fig. 2. Log pseudo first order rate constant vs. log $[P(n\text{-}Bu)_3]$ in reaction with $Co_2(CO)_8$ at 25°C. △, hexane solvent; ○, CH_2Cl_2 solvent.

Reaction of $Co_2(CO)_7P(n-Bu)_3$ with $P(n-Bu)_3$ is about four orders of magnitude slower than reaction of $Co_2(CO)_8$. Furthermore, both $Co_2(CO)_6[P(n-Bu)_3]_2$ and $\{Co(CO)_3[P(n-Bu)_3]_2\}Co(CO)_4$ are formed as products. Thus $Co_2(CO)_7P(n-Bu_3)$ does not appear to be an intermediate in the reaction.

In considering plausible mechanisms it should be kept in mind that the appearance of the ionic product containing disproportionated cobalt requires electron transfer at some stage in the reaction. The overall character of the reaction bears many similarities to a class of organic substitution reactions involving radical anions and free radicals as intermediates [20]. The reaction under consideration here is also closely analogous to the reaction of $Cl_3SnCO(CO)_4$ with various bases L to yield $[Co(CO)_3L_2]Co(CO)_4$ as product. This latter reaction has been assigned a radical chain mechanism on the basis of extensive kinetics and other observations [21]. The corresponding radical chain mechanism for reaction of $Co_2(CO)_8$ with $P(n-Bu)_3$ proceeds as follows [21, 22]:

$$Co_2(CO)_8 + L \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Co_2(CO)_8L \tag{2}$$

$$Co_2(CO)_8L \xrightarrow{k_3} Co(CO)_3L^{\bullet} + Co(CO)_4^{\bullet} + CO \tag{3}$$

$$Co(CO)_3L^{\bullet} + Co_2(CO)_8 \xrightarrow{k_4} Co(CO)_3L^+ + Co_2(CO)_8^{-\bullet} \tag{4}$$

$$Co_2(CO)_8^{-\bullet} \xrightarrow{k_5} Co(CO)_4^- + Co(CO)_4^{\bullet} \tag{5}$$

$$Co(CO)_3L^+ + L \xrightarrow{k_6} Co(CO)_3L_2^+ \tag{6}$$

$$Co(CO)_4^{\bullet} \underset{k_{-7}}{\overset{k_7}{\rightleftharpoons}} Co(CO)_3 + CO \tag{7}$$

$$Co(CO)_3 + L \xrightarrow{k_8} Co(CO)_3L^{\bullet} \tag{8}$$

$$Co(CO)_4^{\bullet} + Co(CO)_3L^{\bullet} \xrightarrow{k_9} Co_2(CO)_7L \tag{9}$$

$$Co(CO)_3L^{\bullet} + Co(CO)_3L^{\bullet} \xrightarrow{k_{10}} Co_2(CO)_6L_2 \tag{10}$$

$$2Co(CO)_4^{\bullet} \xrightarrow{k_{11}} Co_2(CO)_8 \tag{11}$$

The observed ionic product is formed rapidly in steps 5 and 6 following the electron transfer process. The mechanism provides for a rapid chain process, involving equations 4, 5, 7 and 8, which accounts for the fast overall reactions observed. Because the chain process is fast with respect to the competing chain termination steps, equations 9—11, the non-ionic substituted carbonyl dimers are not observed in significant quantities.

There is evidence from several sources that CO loss from the 17-electron carbonyl radical is fast [21, 23]. There is as yet little independent evidence for the outer-sphere electron transfer step, eq. 4, but such a process is a reasonable

means of attaining the observed oxidation—reduction behavior; $Co_2(CO)_8$ has a particularly low reduction potential in comparison with other binary carbonyl compounds [24].

For an idealized radical chain process, in which the rates of termination and initiation can be equated, the reaction would be expected to be 3/2 order in $Co_2(CO)_8$ and first order in $P(n-Bu)_3$ [25]. However, the reaction is too rapid at 25°C for establishment of steady state conditions. Extensive computer modeling, to be reported upon elsewhere [26], reveals that the limiting order in $Co_2(CO)_8$ is about 1.0, as observed, and that the apparent order in phosphine under these conditions is less than one, as observed (Fig. 2). Finally, we note that the slowing of the reaction by addition of O_2 is also consistent with the presence of radical intermediates, as observed in other radical chain processes of metal carbonyls [21, 27]. The formation of a dioxygen adduct with $Co(CO)_4$ has been reported [28].

The present results are important because they provide convincing evidence that radical intermediates are involved in a thermal substitution reaction of $Co_2(CO)_8$. The extraordinary reactivity of $Co_2(CO)_8$ toward substitution, and the unusual product distributions as compared with the binary carbonyls of the other first-row transition elements, are thus accounted for. In addition, the results suggest that radical intermediates are likely to be involved in reactions of $Co_2(CO)_8$ with other substrates, particularly organic compounds.

Acknowledgement

References

1 R.F. Heck, Organotransition Metal Chemistry, Academic Press, New York, 1974.
2 P. Pino, F. Piacenti and M. Bianchi, in I. Wender and P. Pino (Eds), Organic Syntheses via Metal Carbonyls, Vol. 2, Wiley Inc., New York, 1977, p. 43.
3 E.R. Tucci and B.H. Gwynn, J. Amer. Chem. Soc., 86 (1964) 4838.
4 I. Wender, H.W. Sternberg and M. Orchin, J. Amer. Chem. Soc., 74 (1952) 1216.
5 W. Hieber and J. Sedlmeier, Chem. Ber., 87 (1954) 789.
6 W. Hieber and W. Freyer, Chem. Ber., 91 (1958) 1230.
7 A. Sacco and M. Freni, J. Inorg. Nucl. Chem., 8 (1958) 566.
8 J.A. McCleverty, A. Davison and G. Wilkinson, J. Chem. Soc., (1965) 3890.
9 P. Szabo, L. Fekete, G. Bor, Z. Nagy-Magos and L. Marko, J. Organometal. Chem., 12 (1968) 245.
10 A.R. Manning, J. Chem. Soc. A, (1968) 1135.
11 R. Iwanaga, Bull. Chem. Soc. Japan, 35 (1962) 774.
12 W. Hieber, J. Sedlmeier and W. Abeck, Chem. Ber., 86 (1953) 700.
13 V. Yu Gankin, D.P. Krinkin and D.M. Rudlkowski, Zh. Obseh. Khim., 35 (1965) 2127.
14 F. Ungvary, J. Organometal. Chem., 36 (1972) 363.
15 R.F. Heck, J. Amer. Chem. Soc., 85 (1963) 657.
16 P.L. Stanghellini, R. Rossetti, E. Mentasti and E. Pelizzetti, Inorg. Chim. Acta, 22 (1977) 19.
17 F. Basolo and A. Wojcicki, J. Amer. Chem. Soc., 83 (1961) 520.
18 P. Ellgen, Inorg. Chem., 11 (1972) 691.
19 S.E. Rudolph, L.F. Charbonneau and S.G. Smith, J. Amer. Chem. Soc., 95 (1973) 7083.
20 N. Kornblum, Angew. Chem. Intern. Edit., 14 (1975) 734.
21 M. Absi-Halabi and T.L. Brown, J. Amer. Chem. Soc., 99 (1977) 2982.
22 J.K. Kochi, Organometallic Mechanisms and Catalysis, Academic Press, New York, 1978, p. 186.
23 R.W. Wegman and T.L. Brown, J. Amer. Chem. Soc., 102 (1980) 2494.
24 R.E. Dessy, P.M. Weissman and R.I. Pohl, J. Amer. Chem. Soc., 88 (1966) 5117.
25 E.S. Huyser, Free-Radical Chain Reaction, Wiley, New York, 1970.
26 M. Absi-Halabi, J.D. Atwood, N.P. Forbus and T.L. Brown, J. Amer. Chem. Soc., submitted.
27 B.H. Byers and T.L. Brown, J. Amer. Chem. Soc., 99 (1977) 2527.
28 S.A. Fieldhouse, B.W. Fullam, G.W. Neilson and M.C.R. Symons, J. Chem. Soc. Dalton, (1974) 567.