

Figure 4.—Difference CD curves for $[\text{Co}(\text{EDDA})\text{en}]\text{NO}_3 \cdot \text{H}_2\text{O} - [\text{Co}(\text{DEEDDA})\text{en}]\text{I} \cdot \text{H}_2\text{O}$ (—) and $\text{Na}[\text{Co}(\text{EDDA})\text{ox}] \cdot 2\text{H}_2\text{O} - \text{Na}[\text{Co}(\text{DEEDDA})\text{ox}] \cdot 3\text{H}_2\text{O}$ (-----).

metric nitrogens in the *N*-alkyl complexes is supported by the similarity of the CD curves of these complexes and of $C_2\text{-cis}(N)\text{-}[\text{Co}(\text{ox})(\text{gly})_2]^-$ and $C_2\text{-cis}(N)\text{-}[\text{Co}(\text{en})(\text{gly})_2]^+$.⁸ The latter complexes differ from EDDA complexes in that they lack the puckered backbone ring and asymmetric nitrogens of the tetradentate ligand. Studies are currently underway to evaluate the effect of the backbone ring conformation on the

(7) N. Matsuoka, J. Hidaka, and Y. Shimura, *Inorg. Chem.*, **9**, 719 (1970).

(8) N. Matsuoka, J. Hidaka, and Y. Shimura, presented at 18th Symposium on Coordination Chemistry, Sendai, Japan, Sept 1969.

CD spectra of these complexes. On the basis of the work reported here, however, it is likely that the *N*-alkyl-substituted EDDA and the bis-glycinato complexes show similar CD patterns because similar chelate rings are the dominant source of asymmetry in each.

Previous studies^{9,10} of complexes with asymmetric nitrogens have concentrated on cases with no chirality due to the distribution of chelate rings. For such cases it is generally recognized that the asymmetric nitrogens are a major, if not dominant, factor for determining rotational strengths. The results of the present study show that such nitrogens may make a contribution to the asymmetry of a complex with importance comparable to that from the distribution of chelate rings. The contributions of the nitrogens are small for the DMEDDA and DEEDDA ligands where the three R groups on nitrogen are alkyls or substituted alkyls. The contribution is large, however, for EDDA where one R group is hydrogen. Because the effect of an asymmetric donor nitrogen seems to depend upon the effective symmetry of the cobalt(III) chromophore,⁸ such atoms will provide useful information for both experimental and theoretical work with circular dichroism. They may prove important for clarifying previously unexplained changes in CD curves for certain series of compounds.^{11,12} Conversely, they may be valuable for gaining information about structure of complexes from their CD curves.

(9) Much of the work has been recently reviewed: (a) S. F. Mason, *J. Chem. Soc. A*, 867 (1971); (b) C. J. Hawkins, "Absolute Configuration of Metal Complexes," Wiley-Interscience, New York, N. Y., 1971, pp 196-209.

(10) S. Larsen, K. J. Watson, A. M. Sargeson, and K. R. Turnbull, *Chem. Commun.*, 847 (1968).

(11) C. W. Van Saun and B. E. Douglas, *Inorg. Chem.*, **7**, 1393 (1968).

(12) G. R. Brubaker and D. P. Schaefer, *ibid.*, **10**, 970 (1971).

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Kinetics and Mechanism of the Reaction of Dicobalt Octacarbonyl with Alkynes

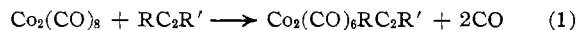
By PAUL C. ELLGEN

Received August 12, 1971

The kinetics of the reaction of dicobalt octacarbonyl with alkynes to give hexacarbonyl- μ -alkyne-dicobalt complexes have been reexamined. In contrast to the previous interpretation that the substitution reaction proceeds by attack of alkyne on a "reactive form" of dicobalt octacarbonyl, the present study proves that this reaction involves dissociation of carbon monoxide to give dicobalt heptacarbonyl, which rapidly adds alkynes.

Introduction

Shortly after the discovery that dicobalt octacarbonyl reacts with alkynes^{1,2} to give hexacarbonyl- μ -alkyne-dicobalt complexes (eq 1), Tirpak and cowork-



ers^{3,4} studied the rate of this reaction in toluene solution and at atmospheric pressure by monitoring the volume of carbon monoxide evolved as a function of

(1) H. W. Sternberg, *et al.*, *J. Amer. Chem. Soc.*, **76**, 1457 (1954).

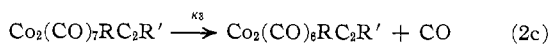
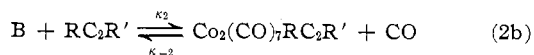
(2) H. Greenfield, *et al.*, *ibid.*, **78**, 120 (1956).

(3) M. R. Tirpak, J. H. Wotiz, and C. A. Hollingsworth, *ibid.*, **80**, 4265 (1958).

(4) M. R. Tirpak, C. A. Hollingsworth, and J. H. Wotiz, *J. Org. Chem.*, **25**, 687 (1960).

time. The rate of CO evolution was found to exhibit a complex dependence on the reagent concentrations. While the reaction rate was sensitive to the concentrations of both reagents, the dependence on the concentration of the alkyne was somewhat weaker than the dependence on dicobalt octacarbonyl concentration. Additionally, evidence for the occurrence of an acetylenic dicobalt heptacarbonyl intermediate was adduced. An elegant analysis resulted in the conclusion that the kinetic data were consistent with the mechanism shown in eq 2 (with $\kappa_{-2} = 0$), where B represents a postulated

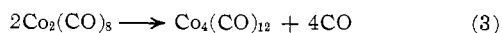




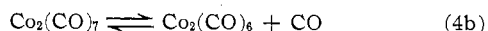
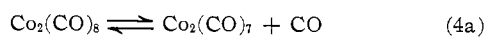
"reactive form" of dicobalt octacarbonyl present in solution at a concentration sufficiently low to be well approximated by a steady-state treatment.

Subsequently, at least two observations have been made which are compatible with the proposal of a direct nucleophilic attack on dicobalt octacarbonyl. Thus, at high temperatures and high pressures of carbon monoxide, dicobalt octacarbonyl absorbs up to 1 additional mol of carbon monoxide.⁵ Similarly, kinetic evidence indicates that the reaction of dicobalt octacarbonyl with triphenylphosphine involves the rapid initial formation of a 1:1 adduct.⁶

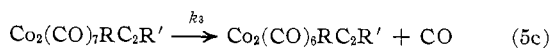
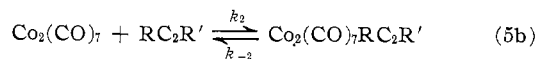
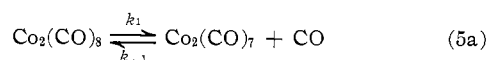
On the other hand, all eight ligands of dicobalt octacarbonyl have been shown to exchange at the same rate with a rate law which is zero order in the concentration of carbon monoxide.^{7,8} Further evidence for a dissociative mechanism is provided by the observation that formation of tetracobalt dodecacarbonyl from dicobalt octacarbonyl (eq 3) follows the rate law⁹ $d[\text{Co}_4(\text{CO})_{12}]/$



$dt = k[\text{Co}_2(\text{CO})_8]^2 P_{\text{CO}}^{-4}$. Since exchange of carbon monoxide occurs readily at temperatures and carbon monoxide pressures where tetracobalt dodecacarbonyl production is insignificant, the successive equilibria shown in eq 4 are indicated.



In view of these observations, an alternative mechanism for reaction 1 can be proposed. This is shown as eq 5. It appears not to have been previously observed



that, at constant CO pressure and under the steady-state assumptions for $[B]$ and $[\text{Co}_2(\text{CO})_7]$, the mechanisms of eq 2 and 5 are kinetically equivalent. Evidence presented below demonstrates that the mechanism of reaction 1 is that shown by (5) and not (2).

It has been shown that dicobalt octacarbonyl exists in solution as an equilibrium mixture of bridged and nonbridged isomers.¹⁰ At room temperature in pentane solution, the equilibrium constant is approximately unity.¹¹ While direct evidence on the rate of interconversion is lacking, it is probable that this process is a rapid one at temperatures in the vicinity of 20°. That interconversions of structures with bridged and nonbridged carbonyl groups are very rapid has been demonstrated¹² in the case of $(\text{C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_4$. In the dis-

(5) S. Metlin, I. Wender, and H. W. Sternberg, *Nature (London)*, **183**, 457 (1959).

(6) R. F. Heck, *J. Amer. Chem. Soc.*, **85**, 657 (1963).

(7) F. Basolo and A. Wojcicki, *ibid.*, **83**, 520 (1961).

(8) S. Breitschaft and F. Basolo, *ibid.*, **88**, 2702 (1966).

(9) F. Ungváry and L. Markó, *Inorg. Chim. Acta*, **4**, 324 (1970).

(10) K. Noack, *Spectrochim. Acta*, **19**, 1925 (1963).

(11) K. Noack, *Helv. Chim. Acta*, **47**, 1064 (1964).

(12) J. G. Bullitt, F. A. Cotton, and T. J. Marks, *J. Amer. Chem. Soc.*, **92**, 2155 (1970).

ussion below, it is assumed that this equilibrium is established very rapidly and hence is without effect on the form of the observed rate law. The symbol " $\text{Co}_2(\text{CO})_8$ " will be used to represent dicobalt octacarbonyl without reference to structure.

Experimental Section

Materials.—All reagents were obtained from commercial sources. The acetylenes (Farchan Research Labs) were used as received; the purity of the 1- and 2-octynes was confirmed gas chromatographically. Dicobalt octacarbonyl (Strem Chemicals, Inc.) was dissolved in hexane at room temperature and recrystallized at -78° before use. While minor contamination by tetracobalt dodecacarbonyl was unavoidable, control experiments with added $\text{Co}_4(\text{CO})_{12}$ established that this impurity had no effect on the observed kinetic behavior. Carbon monoxide (Matheson & Co.) was passed through a trap at -78° before use. Toluene was "analytical reagent" grade.

Kinetic Runs.—The volume of carbon monoxide evolved from reaction mixtures was monitored as a function of time with a thermostated 5-ml gas buret connected to the thermostated reaction vessel by a short length of capillary tubing. A 10–20-ml aliquot of a solution of the more concentrated reagent was introduced into the reaction vessel, and the entire apparatus was purged with CO, bubbled through the vigorously stirred solution, for at least 20 min. Reaction was then initiated by injection of 1.0 ml of a solution of the limiting reagent.

Experiments at reduced pressures were performed as described above, except that all parts of the apparatus which would normally be exposed to the ambient atmospheric pressure were connected (Tygon tubing) to a manifold maintained at a constant reduced pressure by a simple mercury manostat connected to an oil pump. Since only a minimal pumping speed was required, pressure fluctuations could be eliminated by connecting the manostat to vacuum *via* a 2 l. ballast bulb and a short length of glass capillary tubing. Incorporation of a manometer enabled accurate determination of the pressure reduction.

There is no reason to doubt that reaction between alkynes and dicobalt octacarbonyl proceeds quantitatively according to (1) under the conditions of these studies. While the volume of carbon monoxide evolved is invariably somewhat less (2–8%) than that expected from the calculated original dicobalt octacarbonyl concentration, this result is in accord with the difficulty of avoiding contamination of $\text{Co}_2(\text{CO})_8$ by $\text{Co}_4(\text{CO})_{12}$.

Carbon monoxide pressures reported have been corrected for the vapor pressure of toluene.¹³

In toluene at 1 atm pressure, the solubility of carbon monoxide at 10, 20, and 30° was taken as 8.3×10^{-3} , 7.6×10^{-3} , and 7.0×10^{-3} M, respectively.¹⁴ Carbon monoxide solubility has been assumed directly proportional to its partial pressure.

Results and Discussion

The kinetic data reported by Tirpak and coworkers³ for reaction 1 make it exceedingly difficult to imagine an acceptable mechanism for this reaction which is substantially different from those depicted by eq 2 and 5. However, the previously reported data cannot distinguish between these two alternatives, although, clearly, the effect of variations in the solution concentration of carbon monoxide should provide the evidence necessary.

When the concentrations of both reagents are large, with the consequence that the rate of production of $\text{Co}_2(\text{CO})_7\text{RC}_2\text{R}'$ is large, the accumulation of this intermediate makes the analysis of the kinetic data a complex problem. The previous studies were carried out under such conditions. Fortunately for the objectives of the present study, reaction 1 follows pseudo-first-order kinetics when the alkyne and the reaction condi-

(13) R. C. Weast, Ed., "Handbook of Chemistry and Physics," 48th ed, The Chemical Rubber Co., Cleveland, Ohio, p D-128.

(14) W. F. Linke, "Solubilities," Vol. I, 4th ed, Van Nostrand, Princeton, N. J., 1958, p 457; J. H. Hildebrand and R. L. Scott, "The Solubility of Nonelectrolytes," 3rd ed, American Chemical Society Monograph Series, No. 17, Reinhold, New York, N. Y., 1950, p 241; *cf. ref 7.*

tions are judiciously chosen. Thus, at a constant CO pressure, the volume of CO evolved as a function of time gives rise to quite linear plots of $\ln(V_\infty - V)$ vs. time for appropriate, high concentrations of 2-octyne or diphenylacetylene reacting with low concentrations (*ca.* 5 mM) of dicobalt octacarbonyl. This result is readily interpreted as the consequence of reducing the rate at which $\text{Co}_2(\text{CO})_7\text{RC}_2\text{R}'$ is formed to a value sufficiently low that it does not accumulate to a significant extent in the reaction solutions. Moreover, when they occur, departures from first-order behavior, in the form of initial curvature in the kinetic plots, are fully in accord with expectations based on mechanism 5; that is, the initial curvature becomes more noticeable as the concentration of alkyne is increased and that of carbon monoxide is decreased. For 1-octyne, the curvature is more pronounced, and the rate constants reported in Table I are correspondingly less accurate.

TABLE I
RATE CONSTANTS OBSERVED FOR
 $\text{Co}_2(\text{CO})_8 + \text{RC}_2\text{R}' \rightarrow \text{Co}_2(\text{CO})_6\text{RC}_2\text{R}' + 2\text{CO}$

$10^3[\text{Co}_2(\text{CO})_8], M$	$10^2[\text{RC}_2\text{R}']_0, M$	$10^3k_{\text{obsd}}, \text{sec}$	$P_{\text{CO}}, \text{Torr}$	Temp, °C
4.6	4.93 ^c	1.27	718	20
4.6	8.20 ^c	1.89	708	20
4.6	16.3 ^c	3.2	709	20
6.1	42.3 ^c	5.2	718	20
4.8	4.7 ^d	0.63	717	20
4.8	10.0 ^d	1.19	714	20
4.8	19.0 ^d	1.87	717	20
4.8	26.6 ^d	2.52	714	20
5.0	159 ^d	5.3	718	20
4.8	5.1	0.56	720	20
4.8	9.9	0.99	714	20
6.4	23.6	1.78	717	20
4.8	48.2	3.0	719	20
9.3	130	4.4	717	20
2.7	3.94	0.54	527	20
2.0	6.5	0.89	527	20
1.9	10.7	1.29	527	20
3.1	16.7	1.68	527	20
1.6	3.94	0.95	280	20
1.6	6.5	1.45	280	20
1.6	13.3	2.22	280	20
1.6	26.2	3.23	280	20
4.2	5.2	2.04	703	30
4.5	6.8 ^e	2.54	703	30
4.5	6.8 ^f	2.43	703	30
4.2	10.0	3.54	703	30
4.2	20.1	5.8	703	30
4.2	50	8.5	703	30
4.2	10.0	0.221	724	10
4.4	20.1	0.38	724	10
4.4	50	0.65	724	10
4.4	97	1.07	724	10

^a Diphenylacetylene except as otherwise noted. ^b Corrected for the vapor pressure of toluene. ^c 1-Octyne. ^d 2-Octyne. ^e Light excluded. ^f $[\text{Co}_4(\text{CO})_{12}] = 3.8 \times 10^{-2} M$.

The dependence of the pseudo-first-order rate constant on alkyne concentration was studied for 1-octyne, 2-octyne, and diphenylacetylene. For diphenylacetylene the effects of temperature and carbon monoxide concentrations were also investigated. The pseudo-first-order rate constants obtained are reported in Table I.

By inspection of the data in the tables or in Figure 1, it is clear that the rate of (1) decreases very substantially as the concentration of carbon monoxide in solution increases. This is expected from the mechanism of (5). However, Tirpak and coworkers³ successfully

fit their data to the mechanism of (2) under the assumption that formation of $\text{Co}_2(\text{CO})_7\text{RC}_2\text{R}'$ is irreversible (*i.e.*, $\kappa_{-2} = 0$). This assumption is clearly incompatible with the results obtained in the present study; if (2) is to be made consistent with CO inhibition of the reaction rate, the reverse reaction in (2b) must play a significant role in the observed kinetics. The analysis below demonstrates that the observed CO dependence is too strong to be reconciled to the mechanism of eq 2, while a good fit to the requirements of (5) is obtained.

At constant CO concentration, application of the steady-state assumption to the concentrations of B and $\text{Co}_2(\text{CO})_7\text{RC}_2\text{R}'$ for (2) gives the dependence of the pseudo-first-order rate constant shown in eq 6, while the corresponding treatment of eq 5 gives the pseudo-first-order rate constant as shown in eq 7. (k_{obsd} is de-

$$k_{\text{obsd}} = \frac{\kappa_1[\text{RC}_2\text{R}']}{(\kappa_{-1}/\kappa_2) + (\kappa_{-1}\kappa_{-2}/\kappa_2\kappa_3)[\text{CO}] + [\text{RC}_2\text{R}']} \quad (6)$$

$$k_{\text{obsd}} = \frac{k_1[\text{RC}_2\text{R}']}{(k_{-1}/k_2)(1 + k_{-2}/k_3)[\text{CO}] + [\text{RC}_2\text{R}']} \quad (7)$$

defined by $-d[\text{Co}_2(\text{CO})_8]/dt = k_{\text{obsd}}[\text{Co}_2(\text{CO})_8]$. Compare eq 12.) Inversion of either eq 6 or 7 yields the prediction that k_{obsd}^{-1} should be a linear function of $[\text{RC}_2\text{R}']_0^{-1}$ for a particular, constant CO concentration. All of the data collected in this work satisfy this expectation. Figure 1 presents the appropriate plots for

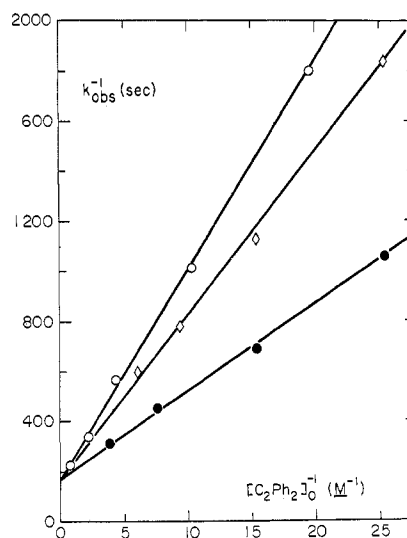


Figure 1.—Reciprocal of observed pseudo-first-order rate constant for reaction 1 plotted vs. the reciprocal of the diphenylacetylene concentration for rate experiments at 20° and three different carbon monoxide concentrations: O, $[\text{CO}] = 7.2 \times 10^{-3} M$; \diamond , $[\text{CO}] = 5.3 \times 10^{-3} M$; \bullet , $[\text{CO}] = 2.8 \times 10^{-3} M$.

TABLE II
SUMMARY OF RATE CONSTANTS

Ligand	Temp, °C	$P_{\text{CO}}, \text{Torr}$	$10^3k_1, \text{sec}$	$\alpha, M \text{ sec}$	$k_{-1}/k_2, M$
1-Octyne	20	713	6.0	29	24
2-Octyne	20	715	6.0	67	56
Diphenylacetylene	20	717	6.0	84	70
Diphenylacetylene	20	528	6.0	66	75
Diphenylacetylene	20	280	6.0	35.2	75
Diphenylacetylene	10	724	2.0	427	108
Diphenylacetylene	30	703	13.7	21.6	46

^a Defined in text. ^b Calculated from eq 9 assuming $k_{-2}/k_3 = 0$.

experiments with diphenylacetylene at three different CO pressures. Table II collects the values of the slopes (α) and reciprocals of the intercepts (k_1 or κ_1) obtained

when the data of Table I are analyzed in this fashion. Extrapolation of the temperature dependence shown in Table II gives a value of $9.4 \times 10^{-3} \text{ sec}^{-1}$ for k_1 at 25° , in good agreement with the value ($11 \times 10^{-3} \text{ sec}^{-1}$) expected from the previous work.³

The difference in kinetic behavior predicted by the steady-state analyses of mechanisms 2 and 5 lies in the CO dependence of the slopes of the reciprocal plots. Letting α be the slope of the reciprocal plot, eq 2 gives

$$\alpha = \frac{\kappa_{-1}}{\kappa_1 \kappa_2} + \frac{\kappa_{-1} \kappa_{-2}}{\kappa_1 \kappa_2 \kappa_3} [\text{CO}] \quad (8)$$

while eq 5 leads to the expectation that α is directly proportional to $[\text{CO}]$ according to

$$\alpha = \frac{k_{-1}}{k_1 k_2} \left(1 + \frac{k_{-2}}{k_3} \right) [\text{CO}] \quad (9)$$

Figure 2 shows a plot of α vs. $[\text{CO}]$ for a series of experiments with diphenylacetylene. To within experimental error, the intercept of this plot is zero; that is, the

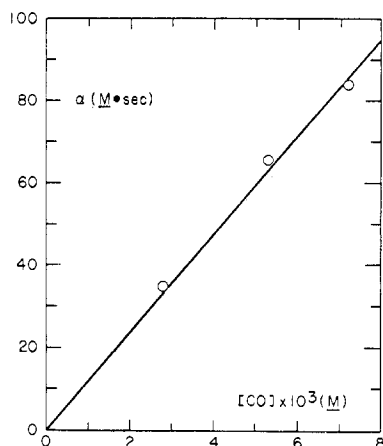
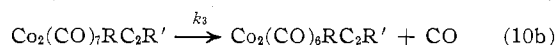
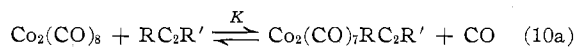


Figure 2.—Plot of slopes of reciprocal plots in Figure 1 vs. carbon monoxide concentration; α , plotted on the ordinate, is defined more completely in the text.

CO dependence is exactly as expected for mechanism 5. Since (5) provides a complete interpretation of the kinetic data while independent evidence for the occurrence of dicobalt heptacarbonyl exists,⁷⁻⁹ it is unnecessary to postulate a species with the characteristics ascribed to B.

Of course, that (5) provides an excellent interpretation of these results does not prove (2) to be incorrect. Either of two rationalizations could render the results in Figure 2 compatible with mechanism 2. First, the intercept could be considered to be small but not zero; values in the range $0 < \kappa_{-1}/\kappa_1 \kappa_2 < 10 \text{ M}^{-1} \text{ sec}^{-1}$ are probably within the experimental error. Alternatively, it could be argued that dicobalt octacarbonyl and the alkyne are always in equilibrium with the alkyneheptacarbonyldicobalt intermediate and carbon monoxide, in which case (2) collapses to the mechanism shown as eq 10 with $K = \kappa_1 \kappa_2 / \kappa_{-1} \kappa_{-2}$. (Since (10) requires that



the rate of (1) be symmetric in the concentrations of alkyne and dicobalt octacarbonyl, it would not be consistent with Tirpak and coworkers' results for 1- and 2-hexyne.³ Fortunately, additional evidence invalidates both of these rationalizations.

The observation of curvature in some of the pseudo-first-order kinetic plots (*vide supra*) is in agreement with the observations of Tirpak and coworkers³ and implies that $\text{Co}_2(\text{CO})_7\text{RC}_2\text{R}'$ accumulates to significant concentrations when the initial reagent concentrations are large. Under these conditions, the rate of formation of $\text{Co}_2(\text{CO})_7\text{RC}_2\text{R}'$ must be significantly larger than its rate of decay. Consider the initial rate of CO evolution. One mole of CO is produced for every mole of $\text{Co}_2(\text{CO})_7\text{RC}_2\text{R}'$ formed. Hence, $dV_{\text{CO}}/dt = (V_s \cdot RT/P_{\text{CO}}) d[\text{Co}_2(\text{CO})_7\text{RC}_2\text{R}']/dt$, where P_{CO} is the CO pressure, T is the absolute temperature, R is the ideal gas constant, V_{CO} is the volume of gaseous CO, and V_s is the volume of the solution. By either mechanism, the initial rate of $\text{Co}_2(\text{CO})_7\text{RC}_2\text{R}'$ decay must be zero. For either mechanism, the initial rate of $\text{Co}_2(\text{CO})_7\text{RC}_2\text{R}'$ formation can be estimated from the data discussed above.

If mechanism 2 is correct, the initial rate of $\text{Co}_2(\text{CO})_7\text{Ph}_2\text{C}_2$ formation is given by (11). Now, at 20° , $\kappa_1 =$

$$\frac{d[\text{Co}_2(\text{CO})_7\text{RC}_2\text{R}']}{dt} = \frac{\kappa_1 [\text{Co}_2(\text{CO})_8] [\text{Ph}_2\text{C}_2]}{(\kappa_{-1}/\kappa_2) + [\text{Ph}_2\text{C}_2]} \quad (11)$$

$6.0 \times 10^{-3} \text{ sec}^{-1}$ and, from Figure 2, an upper limit of $6.0 \times 10^{-2} \text{ M}$ can be put on the ratio κ_{-1}/κ_2 . Use of these values in conjunction with (11) puts a lower limit on the initial rate of CO evolution. The fifth column in Table III presents initial rates calculated in this way

TABLE III
COMPARISON OF INITIAL RATES OF CO EVOLUTION^a

[Co ₂ (CO) ₈], M	[Ph ₂ C ₂], M	Obsd	Initial rates × 10 ³ , l. sec ⁻¹			Steady state
			Eq 5	Eq 2	Calcd	
0.281	0.0135	2.3	2.2	15.9	4.4	
0.213	0.0206	2.7	2.5	16.8	5.0	
0.151	0.0363	3.3	3.1	17.5	6.0	
0.099	0.0897	3.8	4.5	18.2	9.1	

^a Temperature $20.0 \pm 0.1^\circ$; $P_{\text{CO}} = 713 \text{ Torr}$.

for the reagent concentrations investigated experimentally.

If it is assumed that $\text{Co}_2(\text{CO})_7\text{Ph}_2\text{C}_2$ does not accumulate to a significant extent in these initial rate studies, the initial rate of CO evolution will be given by (12),

$$\frac{dV_{\text{CO}}}{dt} = \frac{2V_s RT}{P_{\text{CO}}} \frac{d[\text{Co}_2(\text{CO})_6\text{Ph}_2\text{C}_2]}{dt} = \frac{2V_s RT}{P_{\text{CO}}} k_{\text{obsd}} [\text{Co}_2(\text{CO})_8] \quad (12)$$

where k_{obsd} is to be evaluated according to either (6) or (7); either expression must give essentially the same rate because the values for the various constants must be selected in conformity with the results in Table II and Figure 2. Similarly, the assumption that (10) describes all of the experiments leads to the same expected values for the initial rates. The final column in Table III presents the initial rates calculated from (12) for the experimental reagent concentrations.

Finally, from (5), the initial rate of $\text{Co}_2(\text{CO})_7\text{Ph}_2\text{C}_2$ formation is given by (13). Again, $k_1 = 6.0 \times 10^{-3}$

$$\frac{d[\text{Co}_2(\text{CO})_7\text{Ph}_2\text{C}_2]}{dt} = \frac{k_1 [\text{Co}_2(\text{CO})_8] [\text{Ph}_2\text{C}_2]}{(k_{-1}/k_2) [\text{CO}] + [\text{Ph}_2\text{C}_2]} \quad (13)$$

sec^{-1} and, from Figure 2 and eq 9, an upper limit of 72.0 M can be assigned to the ratio k_{-1}/k_2 by assuming $1 \gg k_{-2}/k_3$. Lower limits to dV_{CO}/dt calculated on

these assumptions for the experimental reagent concentrations are given in the fourth column of Table III.

The experimental results of the initial rate studies are shown in the third column of Table III. These results are in good agreement with those expected on the basis of mechanism 5 if $\text{Co}_2(\text{CO})_7\text{Ph}_2\text{C}_2$ accumulates (fourth column) and in very poor agreement with the requirements of any of the other interpretations (fifth and sixth columns). Therefore, it is concluded that the mechanism of reaction 1 is that given by eq 5.

Because the values for k_1 shown in Table II are obtained by extrapolation, they are not highly accurate; the evaluation at 30° is rendered more inaccurate by the fact that the faster kinetic runs gave relatively severely curved pseudo-first-order rate plots. The temperature dependence given yields estimates for ΔH_1^\ddagger and ΔS_1^\ddagger of 16 ± 2 kcal mol $^{-1}$ and -14 ± 7 eu, respectively. In contrast, the activation parameters reported for CO exchange are $\Delta H_{\text{ex}}^\ddagger = 23 \pm 2$ kcal mol $^{-1}$ and $\Delta S_{\text{ex}}^\ddagger = 13 \pm 4$ eu. Since mechanism 5 suggests that k_1 should also be the rate constant for CO exchange and hence that the same activation parameters should be obtained in both studies, the poor agreement is somewhat disconcerting.

Moreover, the disagreement is too great to be reasonably ascribed solely to experimental error. This point is perhaps best appreciated by a consideration of the rate constants themselves. Over the temperature range $+5$ to -20° , two different reports^{7,8} have given consistent values for the first-order rate constant for CO exchange, while, as noted above, the values for k_1 shown in Table II are in good agreement with the result of earlier studies³ of reaction 1. Nevertheless, extrapolation of the CO exchange results to 20° gives an

estimate of 23×10^{-8} sec $^{-1}$ for the value of k_1 at this temperature.

This apparent discrepancy between the results of the CO-exchange studies and those of the alkyne-substitution studies can be given a plausible explanation. It need only be supposed that *dicobalt heptacarbonyl* also undergoes CO exchange, so that, on the average, more than one molecule of carbon monoxide is exchanged for every event of CO dissociation giving dicobalt heptacarbonyl. Independent evidence exists for the occurrence of reactions 4 (*vide supra*), and these constitute a mechanism of the necessary type if the forward reaction of (4b) is presumed to be sufficiently rapid. (Since the rate of tetracobalt dodecacarbonyl production is proportional to the *equilibrium* constant for (4b) this proposal does not conflict with the observed characteristics of reaction 3. On the other hand, the hypothesis that the rate-determining step of (1) is the reaction of the alkyne with $\text{Co}_2(\text{CO})_6$ can be excluded, since this leads to the prediction that α is proportional to the square of the carbon monoxide concentration.)

That the temperature dependence of k_1 leads to a negative value of ΔS_1^\ddagger is unexpected. However, in view of the uncertainty associated with this value, the unknown role of the dicobalt octacarbonyl isomeric equilibrium in contributing to this value, and the absence of evidence on the structure (or structures) of dicobalt heptacarbonyl, speculation on this result is unwarranted.

Acknowledgment.—Support of this research by the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

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Tertiary Phosphine Complexes of Rhodium(I) and Rhodium(III) Chlorides

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Received June 8, 1971

The most complete series of tertiary phosphine complexes of rhodium yet reported has been prepared. Depending on the particular phosphine and the method of preparation, several different types of complexes may be formed. These include, $\text{RhCl}_3(\text{PR}_3)_3$, $\text{RhCl}(\text{PR}_3)_3$, $\text{RhHCl}_2(\text{PR}_3)_3$, $\text{RhH}_2\text{Cl}(\text{PR}_3)_3$, $\text{RhHCl}_2(\text{PR}_3)_2$, $[\text{RhCl}_2(\text{PR}_3)_2]_2$, $\text{RhClCO}(\text{PR}_3)_2$, $\text{RhCl}_3\text{CO}(\text{PR}_3)_2$, and $\text{RhHCl}_2\text{CO}(\text{PR}_3)_2$. The chemistry involved in the preparation and interconversion of each of these types or classes of complexes is discussed. Their properties, proof of structure, and factors affecting their relative stabilities are also given.

Introduction

A large amount of work has been reported on tertiary phosphine-group VIII transition metal complexes, especially those of triphenylphosphine.¹ The catalytic activity of this type of compound is well known,^{2,3} and they have recently become the object of a great deal of interest by industry particularly with respect to their

use as selective homogeneous catalysts. Because of this the preparation of a series of tertiary phosphine-rhodium chloride complexes was undertaken in the hope that subtle changes could be made in the properties of the compounds while still retaining the same overall features throughout the series. The reaction of rhodium halides with various phosphines, however, results in many different types of complexes, in varying yields, depending on conditions and the properties of the particular phosphine. Although several investigators, most notably Chatt and Shaw, have reported studies

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