In their discussion of the oxidation of Cr(II) in acid solution, Ardon and Plane have proposed an analogous mechanism to explain the formation of binuclear aquo complexes, by molecular oxygen and a variety of other strong "two-electron" oxidants.[10] Most of the oxidants they employed may indeed operate entirely through this mechanism but, with molecular oxygen, a path through a binuclear peroxide might be favored. Tracer experiments using labelled molecular oxygen would test this possibility. It is possible that reaction 5 proceeds stepwise with the intermediate formation of a mononuclear peroxide having the formula $(H_3N)_5Cr-O^*-O^{*+2}$. The idea is attractive because reaction 5 then becomes an integral part of an over-all mechanism, the mononuclear peroxide decomposing to give the products indicated in equation 5 at very low Cr(II) concentrations, but being converted increasingly to the binuclear peroxide at higher Cr(II) concentrations.

In considering the validity of our over-all mechanism, some brief comments may be made regarding the procedure of ignoring reaction paths not yielding the rhodo ion, a course of action which is valid only if these latter reactions do not involve transient intermediates which considerably influence the rhodo-producing reactions. In support of this procedure, it may be noted that the nature of the side reactions is not entirely unknown. Various observations not presented here suggest that these side reactions yield highly soluble

(10) M. A. Ardon and R. A. Plane, THIS JOURNAL, 81, 3197 (1959).

binuclear ions, perhaps entirely analogous in structure to the rhodo ion, but containing a smaller number of ammonia ligands. In terms of the mechanism which has been adopted, such products would not be unanticipated, since they naturally would arise from oxygenation of Cr(II) complexes containing less than five ammonia molecules.[9] Occurrence of such reactions would decrease the stoichiometric yield of rhodo ion but should not cause major changes in the % labelling. One further reason for low yields of rhodo ion might also be mentioned explicitly, since it has bearing on the question of lability of the Cr(IV) oxidation state, a problem of considerable current interest. In our mechanism, it is assumed that the ion $Cr(NH_3)_5$- $(OH)^{+3}$ may exchange oxygen with the water solvent in reaction 2 before reaction 4 occurs, but possible replacement of ammonia by water in the ligand sphere has been ignored. Increase or decrease of ammonia content in $Cr(NH_3)_5(OH)^{+3}$ presumably would eliminate the rhodo ion formed in both reactions 3 and 4, thus decreasing the yield of rhodo ion. Since reaction 3 is the only source of unlabelled rhodo ion, a product of major importance in most experiments, it must be concluded that no major change in ammonia content occurs during the brief period of existence of the $Cr(NH_3)_5(OH)^{+3}$ ion. However, it is possible that the increase in labelling observed in the more alkaline medium employed in experiment 7 of Table I represents a detectable hydrolytic destruction of the $Cr(NH_3)_5$- $(OH)^{+3}$ ion.

Metal Carbonyls. I. Carbon Monoxide Exchange with Nickel Tetracarbonyl and Dicobalt Octacarbonyl[1,2]

BY FRED BASOLO AND ANDREW WOJCICKI[3]

An experimental technique for the investigation of radiocarbon monoxide exchange with metal carbonyls in solution is described. The activation energy for exchange in the system $^{14}CO-Ni(CO)_4$ in toluene is 13 kcal. and the rate of exchange does not depend on the concentration of CO. A dissociation mechanism was therefore assigned to this process. The rates of CO exchange decrease in the order $Ni(CO)_4 > Ni(CO)_3PR_3 > Ni(CO)_2(PR_3)_2$. In $Co_2(CO)_8$ all eight CO's exchange at the same rate via a dissociation mechanism with $E_a = 16$ kcal. Essentially the same results were obtained for the lactone derivative $Co_2(CO)_7(C_7H_8O_2)$, suggesting that only one bridged Co–CO–Co bond need rupture for exchange.

This paper is the first in a series on the investigation of the kinetics and mechanisms of reactions of metal carbonyls and metal carbonyl derivatives. Relatively little quantitative work has been done on these systems.[4-7] Yet they are of considerable im-

portance because of the role that some play as catalysts[8] and because of their relation to the transition metal organometallics and hydrogen compounds.[9] Furthermore, these compounds afford a study of analogous systems having a variety of different coördination numbers and structures. Often with such compounds it is possible to study the reactivity of non-equivalent carbon monoxides in the same compound.

(1) This research was supported in part by a Research Corporation Grant-in-Aid.

(2) Presented in part as paper No. 139 at the XVIIth Congress of the International Union of Pure and Applied Chemistry, Munich, Germany, 1959.

(3) Based upon a portion of a thesis submitted by A. W. to Northwestern University in June 1960, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(4) M. R. Tirpak, J. H. Wotiz and C. A. Hollingsworth, THIS JOURNAL, 80, 4265 (1958).

(5) L. S. Meriwether and M. L. Fiene, ibid., 81, 4200 (1959).

(6) D. F. Keeley and R. E. Johnson, J. Inorg. Nuclear Chem., 11, 33 (1959).

(7) T. H. Coffield, J. Kozikowski and R. D. Closson, International Conference on Coördination Chemistry, London (1959).

(8) I. Wender, H. W. Sternberg and M. Orchin, "Catalysis," P. H. Emmett, Editor, Reinhold Publishing Corp., New York, N. Y., Vol. V, 1957, Ch. 2.

(9) E. O. Fischer and H. P. Fritz, "Advances in Inorganic Chemistry and Radiochemistry," H. J. Emeleus and A. G. Sharpe, Editors, Academic Press, Inc., New York, N. Y., Vol. I, 1959, Ch. 2. G. Wilkinson and F. A. Cotton, "Progress in Inorganic Chemistry," F. A. Cotton, Editor, Interscience Publishers, Inc., New York, N. Y., Vol. I, 1959, Ch. 1.

Reported in this paper are the results of kinetic studies on the exchange of radiocarbon monoxide with $Ni(CO)_4$ and some of its R_3P derivatives, as well as with $Co_2(CO)_8$ and some of its derivatives. In press are papers II on carbon monoxide exchange with cyclopentadienyl metal carbonyls[10] and III with metal carbonyl halides.[11]

Experimental

Compounds and Solvents.—Except for $Ni(CO)_3P(C_6H_5)_3$, which was prepared by the method of Reppe and Schweckendiek,[12] all of the carbonyls used were either generously supplied as free samples, as acknowledged below, or were purchased from commercial sources. The compounds usually were purified and identified by analyses and/or infrared spectra. The $Ni(CO)_4$ purchased from Delta Chemicals was distilled under CO. The $Fe(CO)_5$ purchased from Antara Chemicals was purified by vacuum distillation. Both $Cr(CO)_6$ and $Mn_2(CO)_{10}$ were given to us by Dr. E. O. Brimm of the Union Carbide Corporation. An additional sample of $Mn_2(CO)_{10}$ was supplied by Dr. T. H. Coffield of the Ethyl Corporation. The compound was recrystallized from chloroform before use. Dr. H. W. Sternberg of the U. S. Bureau of Mines furnished samples of $Co_2(CO)_8$, $Co_2(CO)_7(C_7H_8O_2)$ and $Co_2(CO)_6$-($C_6H_5CCC_6$-H_5). Samples of $Ni(CO)_2(P(n$-$C_4H_9)_3)_2$ and $Ni(CO)_2$-$(P(CH_2CH_2CN)_3)_2$ were obtained from Dr. L. S. Meriwether of the American Cyanamid Company.

The solvents used were first purified by the methods described here. Thiophene-free benzene was refluxed over sodium for several hours and then fractionally distilled. The method described by Fieser[13] was used to purify toluene. Chlorobenzene and acetonitrile were dried over Drierite and fractionally distilled. Chloroform was dried over $CaCl_2$ and distilled whereas n-butylamine was dried over KOH and distilled.

The other compounds used were treated as follows. Carbon monoxide of C.P. grade, obtained from Matheson Co., was passed through concentrated sulfuric acid prior to use. Radiocarbon monoxide (1.0 millicurie, 54.3 ml.) purchased from Tracerlab, Inc., was transferred to a two liter storage flask, diluted to one atmosphere with inactive CO, and used in this form. Argon, also from the Matheson Co., was dried with concentrated sulfuric acid. Triphenylphosphine purchased from the Metal and Thermit Corporation was recrystallized from ethanol, whereas $P(n$-$C_4H_9)_3$ from the same source was vacuum distilled and stored under nitrogen. The sample of $P(CH_2CH_2CN)_3$ was used as obtained from Dr. L. S. Meriwether.

Apparatus and Procedure.—The apparatus for studying the exchange between carbon-14 labeled carbon monoxide and metal carbonyls was constructed in a well ventilated hood. It consists of an ordinary vacuum line set-up with the usual attachments to which is connected one of three reaction vessels. One of the vessels is similar in design to that described by Johnson.[14] It was used to make preliminary runs and found to be satisfactory for exchanges with a half-life of more than 2 hr. For extremely slow exchanges a more simple and more adaptable vessel was used. This consisted of a glass tube 12 cm. high and 4 cm. in diameter containing two side arms equipped with stopcocks and sealed at the top with a counting window. These vessels once filled with the reaction mixture were placed in a thermostated bath and the radioactivity of the gas phase was determined over long intervals of time.

Most of the exchange data reported here made use of the reaction vessel and pumping apparatus shown in Fig. 1. The circulatory pump (Model T-6S, Sigmamotor, Inc., Middleport, N. Y.) provided complete circulation and equilibration in the gas phase in less than 2 min., as well as agitation of the solution by means of the gas bubbling through the sintered glass disc. In this way it was possible to study exchange reactions with half-lives as short as 4 min. A thin mica end window Geiger–Muller tube (TGC-2 model,

(10) A. Wojcicki and F. Basolo, *J. Inorg. Nuclear Chem.*, in press.

(11) A. Wojcicki and F. Basolo, THIS JOURNAL, **83**, 525 (1963).

(12) W. Reppe and W. J. Schweckendiek, *Ann.*, **560**, 104 (1948).

(13) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Company, 1941, p. 374.

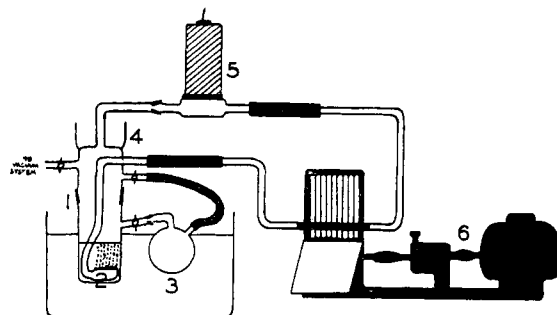(14) R. E. Johnson, *Nucleonics*, **14**, 96 (1956).

Fig. 1.—Apparatus for fast exchange reactions: 1, reaction vessel; 2, sintered glass disc; 3, solution transfer flask; 4, cooled trap; 5, Geiger tube; 6, circulatory pump.

1.8 mg./cm.^{2}, Tracerlab, Inc., Boston, Mass.) was mounted directly above a counting window. This thin window was made of a tough polyester film (Mylar film, Model 31501, Radiation Counter Laboratory, Skokie, Illinois) sealed to glass by means of Shell's Epon Resin mixed with trimethylenediamine. The aluminized surface of the film faced the inside of the apparatus and the total thickness of the window was $1.4 \pm 20\%$ mg./cm.^{2} The Geiger–Müller tube was attached to a conventional scaler and the radioactivity of the gas phase was readily and continuously counted.

A brief summary of procedure for collecting the exchange data is given. A gaseous mixture of CO and Ar of known composition was introduced into a gas buret and approximately 25 ml. of ^{14}CO was added. The apparatus in Fig. 1 was connected to a vacuum line and swept for a period of about 3 hr. with either CO or Ar. It then was evacuated to approximately $1/2$ atm. and the pressure returned to 1 atm. by the addition of a known amount of gas from the buret.

The metal carbonyl solutions were prepared with roughly 30 ml. of solvent saturated with CO or Ar. Solids were weighed under CO and liquids were transferred using micropipets. Aliquots of these solutions were then pipetted into the delivery flask (3, Fig. 1) which was allowed to come to constant temperature before introduction into 2. The zero time count was obtained prior to the transfer of solution, after which counts were taken at different intervals of time. The infinity readings were taken at a period of ten half-lives or by warming the reaction mixture and then returning it to the original temperature. In all cases there was good agreement between the experimental and calculated infinity count.

Temperatures of -10 to $-14°$ were maintained within $\pm 0.5°$ by using ethanol–ice mixtures. Methanol–ice mixture was used for $-20°$ and liquid ammonia for $-33.4°$. Light was excluded in all cases. At the conclusion of each exchange run with a new compound, the infrared spectrum of the solution was determined and compared with a fresh solution of the compound at the same concentration. No decomposition was observed for the systems studied. Duplicate kinetic runs were made with a 10% precision.

Solubility of Carbon Monoxide.—The solubility of CO in benzene, toluene and chloroform at $25°$ is reported in the literature.[15] These were checked and solubilities of CO at other temperatures and in other solvents were determined (Table I). This was done readily in the exchange apparatus described above. Solvent, saturated with CO, was introduced into the exchange vessel containing a known amount of ^{14}CO. From the initial count before introduction of the solution, the equilibrium count and the known capacity of the flask, it was possible to calculate the volume of CO dissolved. The equation

$$A_\infty = \frac{V_G}{V_G + V_S} A_0 \qquad (1)$$

where A_0 is the initial count, A_∞ is the equilibrium count, V_G is the volume of gaseous CO and V_S is the volume of CO dissolved in the solvent was used to determine V_S.

(15) "International Critical Tables," E. W. Washburn, Editor, McGraw-Hill Book Co. Inc., New York, N. Y., Vol. III, 1926, p. 265.
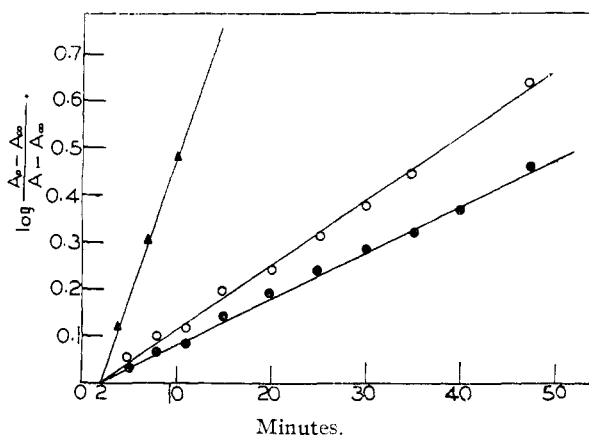
Fig. 2.—Rates of CO exchange with $Co_2(CO)_8$ in toluene at 0.0° as a function of CO concentration: Concentrations in mmoles/l. and in total mmoles are: -●-, $Co_2(CO)_8$, 34.6; $(CO)_s$, 7.6; $(CO)_t$ 6.2. -O-, $Co_2(CO)_8$, 21.7; $(CO)_s$, 3.7; $(CO)_t$, 3.0. -△-, $Co_2(CO)_8$, 20.2; $(CO)_s$, 0.70; $(CO)_t$, 0.6.

TABLE I

SOLUBILITY OF CO IN VARIOUS SOLVENTS

Solvent	Temp., °C.	Sol. (mmole/l.)
Benzene	25.0	6.4
Toluene	31.8	6.7
	25.0	6.8
	0.0	8.0
	-10	8.2
	-20	8.5
	-33.4	8.9
Chlorobenzene	31.8	6.8
Chloroform	25.0	7.6
	-20	9.1
n-Butylamine	0.0	2

Treatment of Data.—All of the exchange reactions investigated were found to follow the McKay[16] equation and give linear plots of log $[A_0 - A\infty /A - A\infty]$ versus time (Fig. 2, where A_0 is the initial radioactivity, A is the radioactivity at time t, and $A\infty$ is the radioactivity at equilibrium. The slope of these lines equals $k_{apparent}/2.303$, which is related to k_{true} by the equation

$$k_{true} = k_{apparent} \frac{xa^{1-\alpha}yb^{1-\beta}}{xa + yb} \quad (2)$$

where a is the concentration of metal carbonyl, b is the concentration of carbon monoxide in solution, x is the number of exchangeable CO's in the metal carbonyl, y is the ratio of total moles of carbon monoxide in the enclosed system to the moles of carbon monoxide in solution, α represents the order in a and β the order in b. Equation (2) is used instead of the usual statistical factor because the carbon monoxide in the experiments was distributed between two phases. Exchange experiments in which a and b are varied permit an estimate of α and β. If $\beta = 0$ then the reaction is assigned an S_N1 or dissociation mechanism whereas if $\beta = 1$ then an S_N2 or displacement path may be involved. The kinetic plots (Fig. 2) show an apparent negative fraction exchange at zero-time instead of passing through the origin. This resulted from using as the zero-time activity, A_0, that measured after 2 min. Such treatment of the data was necessary because of the experimental difficulty that during the initial 2 min. there is a rapid equilibration between the CO in solution and the ^{14}CO in the gas phase.

Results

Qualitative results, in good agreement with the observations of Keeley and Johnson,[3] on the rates

(16) H. A. C. McKay, *Nature*, **142**, 997 (1938).

TABLE II

RATES OF CO EXCHANGE WITH SIMPLE METAL CARBONYLS OF THE FIRST TRANSITION SERIES

Metal carbonyl	Conc., $M(CO)n$ (mmole/l.)	$(CO)_s$ (mmole/l.)	Solvent	Temp. °C.	Exchange
$Ni(CO)_4$	51-76	0.5-8	Toluene	0	Fast[a]
$Co_2(CO)_8$	22-35	0.7-8	Toluene	0	Fast[a]
$Fe(CO)_5$	46	6	Toluene	25	Very slow[b]
	132	1	n Butylamine	0	Slow[c]
$Mn_2(CO)_{10}$	38	7	Toluene	25	Very slow[b]
$Cr(CO)_6$	1	0.3	Toluene	32	Very slow[b]
$V(CO)_6$	22	2 atm.	Heptane	10	Slow[d]

[a] For specific rates see Tables III and V. [b] No detectable exchange in 3 weeks. See ref. 6 where $t^{1/2}$ for $Fe(CO)_5$ is reported > 4 yr. and for $Mn_2(CO)_{10}$ > 10 yr. Detailed exchange studies on $Cr(CO)_6$ in the gas phase at 108-135° were made by G. Pajaro, F. Calderazzo and R. Ercoli (to be published in Gazz. chim. ital.). [c] No detectable exchange in 3 hr. This result is not in agreement with the existence of $[Fe(CO)_6]^{+2}$ (H. W. Sternberg, R. A. Friedel, S. L. Shufler and I. Wender, THIS JOURNAL, **77**, 2675 (1955)) which is expected to exchange CO rapidly. However it is in agreement with more recent studies (W. Hieber and H. Kuhlen, *Ber.*, **91**, 2223 (1958)) and it should also be noted that investigations on the systems $Fe(CO)_5$– amines continue (W. F. Edgell, private communication). [d] Exchange with $t^{1/2} \sim 7$ hr., G. Pajaro, F. Calderazzo, R. Ercoli, private communication.

TABLE III

RATES OF CO EXCHANGE WITH $Ni(CO)_4$ IN TOLUENE[a]

Conc. $(CO)_4$[b] Ni(CO)_4 (mmole/l.)	$(CO)_s$[b]	$(CO)_t$[c]	Temp., °C.	$k_{apparent}$ (sec.$^{-1}$) $\times 10^4$	k (sec.$^{-1}$) $\times 10^4$
50.7	6.4	6.2	25.0	>30	>60
50.7	7.6	6.2	0.0	3.2	6.4
76.0	7.6	6.2	0.0	4.8	7.7
50.7	4.1	3.3	0.0	5.5	7.8
50.7	0.45	0.36	0.0	~42	~9.5
50.7	7.8	6.2	-10	1.6	3.2
50.7	7.9	6.2	-14	1.0	2.0

[a] $Ea = 13$ kcal. [b] Mmoles/l. of dissolved CO. [c] Total mmoles of CO in enclosed system.

of radiocarbon monoxide exchange with some metal carbonyls in solution are given in Table II. Kinetic plots for the exchange of $Co_2(CO)_8$ in toluene solution as a function of CO concentration are shown in Fig. 2. Data on the exchange of $Ni(CO)_4$ are tabulated in Table III, on its R_3P derivatives in Table IV, and on $Co_2(CO)_8$ and its derivatives in Table V.

Discussion

As shown in Table II, the exchange of radiocarbon monoxide with the simplest first row transition metal carbonyls in solution is extremely slow at room temperature for $Cr(CO)_6$, $Mn_2(CO)_{10}$ and $Fe(CO)_5$, whereas it is very fast for $Co_2(CO)_8$ and $Ni(CO)_4$. Similar observations were made with cyclopentadienyl metal carbonyls where it was found that $C_5H_5V(CO)_4$, $(C_5H_5)_2Mo_2(CO)_6$, $C_5H_5Mn(CO)_3$ and $(C_5H_5)_2Fe_2(CO)_4$ exchange extremely slowly, and $C_5H_5Co(CO)_2$ and $(C_5H_5)_2Ni_2(CO)_2$ exchange rapidly.[10] It is also of interest to note that much the same trend was observed for the exchange of cyanide with transition metal cyanide complexes,[17] e.g. $Cr(CN)_6^{-3}$, $Fe(CN)_6^{-3}$, $Fe(CN)_6^{-4}$ and $Co(CN)_6^{-3}$ exchange slowly, whereas $Ni(CN)_4^{-2}$, $Pd(CN)_4^{-2}$ and $Hg(CN)_4^{-2}$ exchange rapidly.

(17) A. W. Adamson, J. P. Welker and M. Volpe, THIS JOURNAL, **72**, 4030 (1950).

TABLE IV

RATES OF CO EXCHANGE WITH $Ni(CO)_3P(C_6H_5)_3$ AND WITH "$Ni(CO)_2(PR_3)_2$" AT 25.0°

Complex	Conc. (mmole/l.)					$k_{apparent}$ (sec.$^{-1}$) $\times 10^5$
	Complex	$(CO)_s{}^a$	$(CO)_t{}^b$	PR_3	Solvent	
$Ni(CO)_3P(C_6H_5)_3$	37.8	6.2	5.9	...	Toluene	47 (8.9)^c
	31.2	1.6	1.5	...	Toluene	140 (14)^c
	14.3	1.6	1.5	...	Toluene	62 (9.9)^c
$Ni(CO)_2(P(C_6H_5)_3)_2$	13.9	6.4	2.9	...	Benzene	15
	14.2	6.4	2.9	140	Benzene	2.3
	14.2	6.4	2.9	320	Benzene	1.5
$Ni(CO)_2P(n-C_4H_9)_3)_2$	11.2	6.4	2.9	...	Benzene	2.5
	11.2	6.4	2.9	130	Benzene	1.4
$Ni(CO)_2(P(C_2H_4CN)_3)_2$	15.9	?^{d}	~3	...	Acetonitrile	25
	15.9	?^{d}	~3	160	Acetonitrile	2.0

^{a} Mmoles/l. of dissolved CO. ^{b} Total mmoles of CO in the enclosed system. ^{c} Values in parentheses are for k_{true} (sec.$^{-1}$) $\times 10^4$. ^{d} Concentration of CO corresponds to a saturated solution at 25° and 1 atm.

TABLE V

RATES OF CO EXCHANGE WITH $Co_2(CO)_8$ AND WITH TWO OF ITS DERIVATIVES IN TOLUENE

| Compound	Conc. (mmole/l.)			Temp., °C.	$k_{apparent}$ (sec.$^{-1}$) $\times 10^4$	k_{true} (sec.$^{-1}$) $\times 10^4$
	Compound	$(CO)_s{}^a$	$(CO)_t{}^b$			
$Co_2(CO)_8{}^c$	34.6	7.6	6.2	0.0	3.8	13
	20.2	0.70	0.57	0.0	23	19
	21.7	3.7	3.0	0.0	5.3	15
	40.0	0.75	0.58	-20	2.0	0.90
$Co_2(CO)_7(C_7H_5O_2)^d$	15.5	3.0	2.4	0.0	2.8	8.4
	15.5	0.70	0.57	0.0	9.8	10
	27.6	0.75	0.58	-20	0.72	0.45
$Co_2(CO)_6(C_6H_5CCC_6H_5)$	18.7	6.4	2.8	25	0.01	...

^{a} Mmoles/l. of dissolved CO. ^{b} Total mmoles of CO in the enclosed system. ^{c} E_a = 16 kcal.; all 8 CO's exchange at the same rate. ^{d} E_a = 20 kcal; all 7 CO's exchange at the same rate.

Thus it is seen that the rate of exchange of CO and of its isoelectronic CN^- with metal carbonyls and with metal cyanides, respectively, appears to increase abruptly with increasing atomic number of the transition metal. This is also generally accompanied by a decrease in coördination number. The rapid exchange of $Ni(CN)_4^{-2}$, $Pd(CN)_4^{-2}$ and $Hg(CN)_4^{-2}$ has been attributed to a low energy bimolecular displacement process. This seems plausible, since species of higher coördination number such as $Ni(CN)_5^{-3}$ and $Ni(CN)_6^{-4}$ have been reported.[18] Still it would be of interest to determine the rate of exchange as a function of cyanide ion concentration by some fast reaction technique.

It has also been suggested[6] that the rapid exchange of $Ni(CO)_4$ is due to a nucleophilic displacement by CO. This too seems plausible because of the high nuclear charge on nickel and of the low coördination number. However, the results reported here clearly show that exchange in the system $Ni(CO)_4$–^{14}CO does proceed by a dissociation mechanism. Similar studies are in progress[19] on the systems $Co(NO)(CO)_3$–^{14}CO and $Fe(NO)_2(CO)_2$–^{14}CO.

Nickel Tetracarbonyl.—The results of kinetic studies on the exchange of radiocarbon monoxide with nickel tetracarbonyl in toluene solution show that the exchange rate does not depend on the concentration of carbon monoxide (Table III). This supports a dissociative path for exchange

$$Ni(CO)_4 \rightleftharpoons Ni(CO)_3 + CO \qquad (3)$$
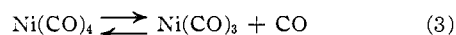
Such a process is in accord with the kinetic studies of Garratt and Thompson[20] on the thermal decomposition of $Ni(CO)_4$ in the gas phase. They report an activation energy of "somewhat greater than 12 kcal." for dissociation (3), in good agreement with the value of 13 kcal. obtained for exchange in toluene solution. It is also of interest to note that the nickel phosphine carbonyls were found to react with phosphines by a dissociation mechanism.[5]

One can speculate as to why these tetrahedral compounds react by an S_N1 rather than an S_N2 process. First, it should be remembered that unlike tetrahedral carbon compounds, the nickel(0) compounds are d^{10} systems and the filled d orbitals may offer appreciable repulsive interaction to any attacking nucleophilic reagent. Secondly, the geometry of the d orbitals is such that for a tetrahedral structure only the $d_{x^2-y^2}$ and the d_{z^2} orbitals can efficiently π-bond with the vacated p orbital on the ligand atom. This means that in $Ni(CO)_4$ there is a total of two π-bonds to distribute among four Ni–C bonds. Kimball[21] calculated that there are three strong π-orbitals available for overlap with the ligand atoms in a triangular planar structure (sp^2). In an sp^2 $Ni(CO)_3$ intermediate, two of these π-orbitals are filled and can participate in bonding. Thus the driving force for a dissociative exchange path may be the stabilization effect of π-bonding in the transition state.

(18) C. M. Harris, R. S. Nyholm and N. C. Stephenson, *J. Chem. Soc.*, 4375 (1956); M. S. Blackie and V. Gold, *ibid.*, 4033, 4037 (1959).

(19) A. T. Brault, private communication.

(20) A. P. Garratt and H. W. Thompson, *J. Chem. Soc.*, 1822 (1934).

(21) G. E. Kimball, *J. Chem. Phys.*, **8**, 188 (1940).

Cotton, Fischer and Wilkinson[22] report the enthalpies of the reaction

$$M(CO)_n{}^{(g)} \longrightarrow M^{(g)} + n(CO)^{(g)} \qquad (4)$$
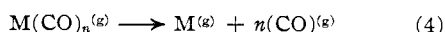
for M = Cr, Fe and Ni. They calculated average bond energies of 27.1, 27.7 and 35.2 kcal. for Cr-$(CO)_6$, $Fe(CO)_5$ and $Ni(CO)_4$, respectively. These values are inconsistent with the observation that the dissociative exchange of $Ni(CO)_4$ is fast whereas that of $Fe(CO)_5$ and $Cr(CO)_6$ is extremely slow. However, the above thermochemical data for equation (4) are for the ground states of $M_{(g)}$ and $CO_{(g)}$, which means 3 $d^5 4s^1$ for Cr, 3 $d^6 4s^2$ for Fe and 3 $d^8 4s^2$ for Ni. For an S_N1 exchange process, the metal in the transition state is perhaps in about the same valency state as it is in the compound. On this basis values of average bond energies of 55, 58 and 46 kcal. for $Cr(CO)_6$, $Fe(CO)_5$ and $Ni(CO)_4$, respectively, were estimated[23] assuming valency states of d^6, d^8 and d^{10}, respectively. Similar estimates including also due allowance for an assumed excited state of CO gave values of 87, 89 and 77 kcal.[22] Because of the uncertainties in these values they should be given only qualitative significance. However, this treatment does show that the Ni-C bond is weaker than either the Fe-C or Cr-C bonds in these metal carbonyls. This then is in agreement with their rates of carbon monoxide exchange.

The estimated average bond energy of 42–77 kcal. for the Ni-C bond in $Ni(CO)_4$ is much larger than the activation energy of 13 kcal. for carbon monoxide exchange. This can only be understood if the energy required for the rupture of the first Ni-C bond is much less than the average bond energy. There is some chemical evidence in support of this. For example, it is known that two of the CO's in $Ni(CO)_4$ are readily replaced to form $Ni(CO)_2L_2$ but that the last two are much less reactive.[24] Such behavior has been explained on the basis that the two π-bonds available to these tetrahedral compounds become largely localized on the Ni-C bonds of the last two CO's. Thus each Ni-C bond in $Ni(CO)_2L_2$ contains essentially a complete π-bond and is stronger than the Ni-C bond in $Ni(CO)_4$ which has only effectively half of a π-bond. It may also be added that in the gas phase decomposition of $Ni(CO)_4$, one CO comes off more readily than the other three.[20]

This is further supported by a comparison of the data in Table III with the data in Table IV. These data clearly show that the rate of radio-carbon monoxide exchange decreases in the order $Ni(CO)_4 > Ni(CO)_3PR_3 > Ni(CO)_2(PR_3)_2$. The ratio of rates for $Ni(CO)_4$: $Ni(CO)_3P(C_6H_5)_3$: $Ni(CO)_2(P(C_6H_5)_3)_2$ at 25° are approximately 420: 70:1. The last value may be less than 1, but this is the best estimate possible on the basis of the available data. The value chosen is that determined in the presence of a large excess of $P(C_6H_5)_3$ where the equilibrium
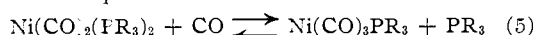
$$Ni(CO)_2(PR_3)_2 + CO \rightleftharpoons Ni(CO)_3PR_3 + PR_3 \qquad (5)$$

is largely shifted to the left. Because of this complication no attempt was made to determine the rate dependence on CO concentration for $Ni(CO)_2$-$(PR_3)_2$ systems. However, the data do show that the exchange of $Ni(CO)_3P(C_6H_5)_3$ does not depend on the concentration of CO. One final point is that the rate of CO exchange found for $Ni(CO)_3$-$P(C_6H_5)_3$ is in good agreement with that reported for the reaction[6]

$$Ni(CO)_3P(C_6H_5)_3 + P(C_6H_5)_3 \longrightarrow$$
$$Ni(CO)_2(P(C_6H_5)_3)_2 + CO \qquad (6)$$
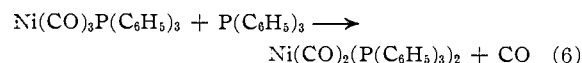
This is to be expected, since both exchange and reaction are believed to go by a dissociation process involving essentially $Ni(CO)_2P(C_6H_5)_3$.

Dicobalt Octacarbonyl.—Data in Table V show that the rate of carbon monoxide exchange with $Co_2(CO)_8$ and with its lactone derivative Co_2-$(CO)_7(C_7H_8O_2)$ is rapid and does not depend on the concentration of CO. This suggests that the exchange proceeds by a dissociative rate determining path. Such a result is in agreement with the dissociation process proposed to account for the absorption of one mole of CO by one mole of Co_2-$(CO)_8$.[25]

It was previously suggested[6] that exchange in the system $Co_2(CO)_8$–^{14}CO may involve first a rapid equilibration to form two equivalents of the free radical $Co(CO)_4\cdot$, which in turn undergoes a rate determining S_N2 exchange with ^{14}CO. Such a mechanism can be ruled out on two accounts. First, the rate of exchange was found not to depend on the concentration of CO. Second, even if the radical $Co(CO)_4\cdot$ should undergo exchange by a dissociative process, the rate would be proportional to the square root of the concentration of $Co_2(CO)_8$ and not its first power as was found.

Additional evidence against a possible initial dissociation of the dimer into monomer comes from the observation that $Co_2(CO)_7(C_7H_8O_2)$ undergoes exchange at about half the rate of $Co_2(CO)_8$ exchange and with about the same energy of activation. Mills and Robinson[26] have shown that these compounds have only one carbonyl bridge and are lactone derivatives with the structure

It is difficult to see how such a compound could undergo cleavage to yield reactive monocobalt species. Unlike either of these two cobalt compounds, $Co_2(CO)_6(C_6H_5CCC_6H_5)$ undergoes exchange of ^{14}CO at an extremely slow rate. Sly[27] has found that this acetylene derivative has the structure
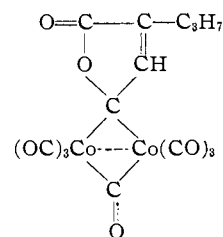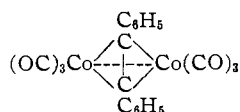
(22) F. A. Cotton, A. K. Fischer and G. Wilkinson, THIS JOURNAL, **81**, 800 (1959).

(23) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 63.

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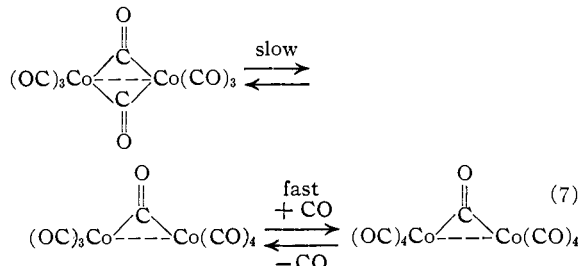(25) S. Metlin, I. Wender and H. W. Sternberg, *Nature*, **183**, 457 (1959).

(26) O. S. Mills and G. Robinson, *Proc. Chem. Soc.*, 156 (1959).

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Therefore it would appear that at least one carbonyl bridge is required for the rapid exchange of CO in these binuclear cobalt systems.

In keeping with these observations, a possible mechanism may be

Since all eight CO's exchange at the same rate (Fig. 2), it is necessary that free rotation about the cobalts in the active intermediates be assumed possible. The reaction between 1- and 2-hexyne and $Co_2(CO)_8$ was investigated[4] and it was postulated that these reactions may involve a reactive biradical intermediate. On this basis, it is possible that the CO exchange may follow the reaction scheme (8). These two mechanisms are very similar and cannot be distinguished with the data now available. Other mechanisms, also in accord with the experimental observations, could be cited but this would serve no useful purpose because the details of the
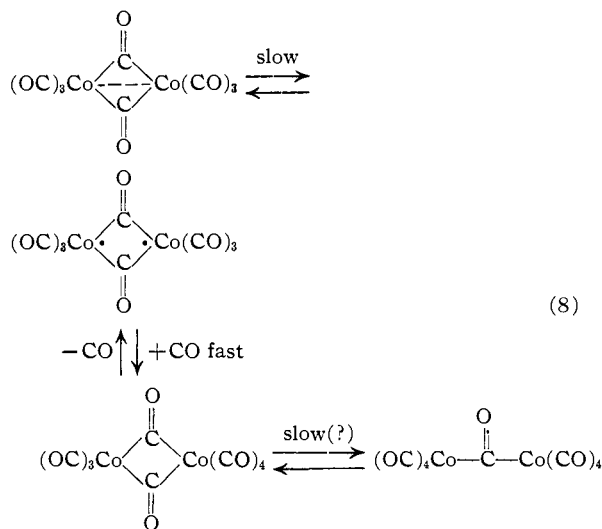
exchange process cannot yet be assigned. The two mechanisms proposed are intended to represent in a general way the type of process that is perhaps involved and both are consistent with the existence of $Co_2(CO)_9$.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NORTHWESTERN UNIVERSITY, EVANSTON, ILLINOIS]

Metal Carbonyls. III. Carbon Monoxide Exchange with Some Metal Carbonyl Halides[1,2]

BY ANDREW WOJCICKI[3] AND FRED BASOLO

Kinetic studies on the exchange of ^{14}CO with metal carbonyl halides in solution are reported. The exchange of $Mn(CO)_5X$ proceeds by an S_N1 path whereas that of $Fe(CO)_4I_2$ involves an S_N2 mechanism. The relative rates of exchange of the $Mn(CO)_5X$ compounds decrease in the order: $Mn(CO)_5Cl > Mn(CO)_5Br > Mn(CO)_5I$. This same order was found for $C_5H_5Fe(CO)_2X$; moreover, $C_5H_5Fe(CO)_2I > C_5H_5Fe(CO)_2CN$. The exchange for some square planar compounds was too fast to measure.

The kinetics and mechanism of carbon monoxide exchange with metal carbonyls[4,5] and with cyclopentadienyl metal carbonyls[1] were reported recently. This paper describes the investigation of ^{14}CO exchange with solutions of $Mn(CO)_5X$, $C_5H_5Fe(CO)_2X$, $Fe(CO)_4I_2$, $Rh_2(CO)_4Cl_2$, $Rh(P-(C_6H_5)_3)_2COCl$ and $Pt_2(CO)_2Cl_4$.

Experimental

Compounds and Solvents.—The metal carbonyl halides used in this study are all known compounds. They were prepared by the methods described in the literature and characterized by analyses and/or infrared spectra.[6] We also wish to acknowledge the gift of a sample of $C_5H_5Fe(CO)_2Br$ by Professor E. O. Fischer and of a sample of $Rh_2(CO)_4Cl_2$ by Dr. H. W. Sternberg. The solvents used were all puri-

(1) For paper II on cyclopentadienyl carbonyls see A. Wojcicki and F. Basolo, *J. Inorg. Nuclear Chem.*, in press.

(2) Presented in part as paper No. 139 at the XVIIth Congress of the International Union of Pure and Applied Chemistry, Munich, Germany, 1959.

(3) Based upon a portion of a thesis submitted by A. W. to Northwestern University in June 1960, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(4) D. F. Keeley and R. E. Johnson, *J. Inorg. Nuclear Chem.*, **11**, 33 (1959).

(5) F. Basolo and A. Wojcicki, THIS JOURNAL, **83**, 520 (1961).

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