The temperature was kept at 25 ± 1° during the titration, a water-bath surrounding the titration vessel being employed when necessary. Stirring was accomplished by a Teflon coated magnetic stirring bar. The reference solution was 0.05 *M* potassium hydrogen phthalate for which the value *p*H 4.00 was taken. A secondary standard chosen to ensure reproducible operation of the electrodes in the high *p*H range was 0.05 *M* NH_4NO_3 in molar ammonia for which the value *p*H 10.63 was repeatedly observed. Deviation from this value for the secondary standard indicated that rejuvenation of the electrodes was required.

Two titrations were required to secure data leading the calculation of $\overline{n}$, the degreee of hydroxo complexing by ammine-copper species. A solution containing ammonia and ammonium nitrate was titrated potentiometrically with NaOH and a second solution containing in addition cupric nitrate was similarly titrated. In order to maintain the desired ammonia activity during the titrations, the following steps were required: first, the free ammonia concentration was initially adjusted to $1 + 4.2 \times C_{Cu}$ secondly, the titration was conducted using normal sodium hydroxide solution; and finally, after the addition of NaOH equivalent to the ammonium nitrate each subsequent addition of alkali was accompanied by the addition of an equal volume of 2 *M* NH_3. These conditions resulted in maintaining the ammonia activity essentially unchanged except for the small amount liberated from the amminecopper species upon complexing with hydroxide ions. Where the concentration of copper with respect to ammonia was small this uncertainty became negligible.

A similar technique was employed to obtain data for the calculation of chelation constants except that here both of the titrated solutions contained the cupric nitrate and one contained in addition the diol-containing substance.

In calculating the k_a values for the diols, corrections to allow for the activity of sodium hydroxide were applied.[2]

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

Metal Carbonyls. IV. Kinetics of the Reaction of Manganese Pentacarbonyl Halides with a Variety of Ligands

BY ROBERT J. ANGELICI AND FRED BASOLO

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The reaction in solution of $Mn(CO)_5X$ with various reactants L was found to yield the monosubstituted derivative $Mn(CO)_4LX$, where X = Cl, Br, I and L = $P(C_6H_5)_3$, $As(C_6H_5)_3$, $Sb(C_6H_5)_3$, C_2H_5NC, $P(C_6H_5)Cl_2$, $P(OC_4H_9)_3$, $P(OCH_2)_3CCH_3$ and $P(OC_6H_5)_3$. Under similar conditions when L = $P(C_4H_9)_3$, C_5H_5N, $C_6H_5NH_2$, *p*-$CH_3C_6H_4NH_2$ and *o*-$CH_3C_6H_4NH_2$, the disubstituted derivative $Mn(CO)_3L_2X$ was obtained. Kinetic studies show that the rates of reaction depend neither on the nature of L nor its concentration. The rates decrease with increasing atomic number of X and also decrease slightly with increasing polarity of the solvent. The reactions are assigned a dissociation mechanism. The infrared absorption wave numbers of the carbonyl groups of the products are reported.

The kinetics and mechanism of carbon monoxide exchange with $Mn(CO)_5X$ were reported recently.[1] It has also been found that $Mn(CO)_5X$ reacts with several reagents in the absence of solvent at 120° to yield disubstituted products of the type $Mn(CO)_3L_2X$.[2] The preparation of a monosubstituted product, $Mn(CO)_4P(C_6H_5)_3I$, was mentioned earlier.[3] The present paper reports the formation of $Mn(CO)_4LX$ by the reaction between $Mn(CO)_5X$ and L in solution at room temperature. Kinetic studies are reported for the reaction

$$Mn(CO)_5X + L \longrightarrow Mn(CO)_4LX + CO \quad (1)$$

Experimental

Preparation and Purification of Materials.—The $Mn_2(CO)_{10}$ was a gift from Dr. T. H. Coffield of the Ethyl Corporation. With it as a starting material, $Mn(CO)_5Cl$[2], $Mn(CO)_5Br$[2] and $Mn(CO)_5I$[4] were prepared as described in the literature and identified by their infrared spectra.

The triphenylphosphine (m.p. 79–80°) and triphenyl phosphite were obtained from the Matheson, Coleman and Bell Co., triphenylarsine, triphenylstibine, aniline and *p*-toluidine from the Eastman Kodak Co., tributylphosphine from the Westvaco Co., and tributylphosphite and phenyldichlorophosphine from the Victor Chemical Works. All were used without further purification. The ethyl isocyanide, *o*-toluidine and *o*-chloroaniline from Eastman Kodak were distilled at 78–80°, 197° and 205–206°, respectively. The preparation and purification of 1-methyl-phospha-3,5,8-trioxabicyclo[2.2.2]octane, $P(OCH_2)_3CCH_3$, was carried out by Mr. Smith Holt as reported.[5] Toluene and chloroform were purified according to Fieser.[6] Carbon tetrachloride, benzene and nitrobenzene were dried over calcium chloride and distilled; nitromethane was washed twice with aqueous sodium hydrogen carbonate, dried over calcium chloride and distilled; acetone was dried over potassium carbonate and distilled. Other solvents used were of reagent grade.

Determination of Rates.—The rates were determined by following the disappearance of the higher frequency carbonyl absorption of $Mn(CO)_5X$ as it reacted with L to form $Mn(CO)_4LX$. A Baird-Associates Model 4–55 double beam recording spectrophotometer with NaCl optics was used to follow the reactions as well as to determine the product absorptions in the carbonyl stretching region. A polystyrene standard was used for calibration.

An aluminum foil-wrapped round bottom flask containing a 5 ml. solution of $Mn(CO)_5X$ and a flask containing a 5 ml. solution of the ligand, L, were thermostated in a constant temperature bath. At zero time the ligand solution was poured into the foil-wrapped flask and mixed well. A sample of this solution was withdrawn with an eye-dropper and placed in an infrared cell. The spectrum of this sample was then taken in the carbonyl region using a solvent reference. Figure 1 illustrates a typical series of spectra taken at different times. From the transmittances, linear plots of $\ln (A - A_\infty)$ *versus* time were obtained and the first order rate constants were calculated from the slopes of these lines. In these calculations, A is the absorbance, at time *t*, and A_∞, the absorbance at $t = \infty$. The A_∞ used was that measured experimentally and was almost zero in all cases except for $Mn(CO)_5I$ where the reactions did not go to completion. Then $A_\infty = 0$ was assumed and the rate constants were calculated from the initial first order slope before the reverse rate became significant. The maximum deviation of the calculated rate constants was ± 3%, except for the reactions involving ethyl isocyanide where the deviation was ±6.5%. It should be noted that the variations of the absorption intensities with concentrations of manganese

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(1) A. Wojcicki and F. Basolo, *J. Am. Chem. Soc.*, **83**, 525 (1961).

(2) E. W. Abel and G. Wilkinson, *J. Chem. Soc.*, 1501 (1959).

(3) W. Schropp, Jr., Doctorate Thesis, Technische Hochschule Munchen, 1960, referred to in W. Hieber, W. Beck and H. Tengler, *Z. Naturforschg.*, **15b**, 411 (1960).

(4) E. O. Brimm, M. A. Lynch, Jr., and W. J. Sesny, *J. Am. Chem. Soc.*, **76**, 3831 (1954).

(5) J. G. Verkade and L. T. Reynolds, *J. Org. Chem.*, **25**, 663 (1960).

(6) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Company, New York, N. Y., 1957, pp. 283, 292.

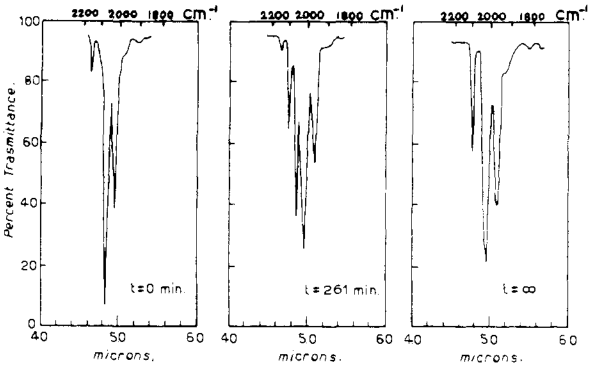

Fig. 1.—Infrared spectra of the reaction of $Mn(CO)_5Br$ with $P(C_6H_5)_3$ in chloroform at 30.1°.

pentacarbonyl halides in these systems follow the Beer–Lambert law. None of the reactions was found to exhibit light catalysis except that involving $P(C_4H_9)_3$. No explanation for its anomalous behavior is apparent.

Product Identification. The reactions of $Mn(CO)_5X$ with an excess of $As(C_6H_5)_3$ in chloroform solution were observed to evolve one CO per $Mn(CO)_5X$. This is in accord with equation 1. The product, $Mn(CO)_4LX$, was not soluble in water, as might be expected for an ionic compound, and did not readily precipitate AgX on the addition of alcoholic $AgNO_3$. The fact that the conductivity did not change during the reaction also indicates that ions are not formed. The infrared spectra of the reaction mixtures at the completion of the reaction do not correspond to the known disubstituted products. Direct evidence that the reaction products are the $Mn(CO)_4LX$ compounds was obtained by isolation and analysis of three different compounds. These compounds had the same infrared spectra as did the corresponding reaction mixture of the kinetic runs at infinite time. It was not possible to isolate the products under the reaction conditions for the kinetic studies because of the large excess of the ligand, L, present.

The compound, $Mn(CO)_4P(C_6H_5)_3Cl$, was isolated from a reaction mixture of 0.094 g. of $Mn(CO)_5Cl$ and 0.11 g. of $P(C_6H_5)_3$ in 5 ml. of chloroform. After it was allowed to stand for 24 hrs. at room temperature, the chloroform was evaporated under a stream of air. The yellow product was then recrystallized twice by dissolution into *n*-hexane at room temperature and crystallization at dry-ice temperatures.

Anal. Calcd. for $Mn(CO)_4P(C_6H_5)_3Cl$: C, 56.9; H, 3.23. Found: C, 56.7; H, 3.50.

This same procedure was used to prepare $Mn(CO)_4As(C_6H_5)_3Cl$. A chloroform solution of 0.057 g. of $Mn(CO)_5Cl$ and 0.079 g. of $As(C_6H_5)_3$ was allowed to react at room temperature for 24 hrs. after which the desired product was isolated and purified.

Anal. Calcd. for $Mn(CO)_4As(C_6H_5)_3Cl$: C, 51.9; H, 2.95. Found: C, 51.1; H, 3.08.

The reaction between 0.11 g. of $Sb(C_6H_5)_3$ and a slight excess of $Mn(CO)_5Br$ (0.094 g.) in chloroform solution at 40° for 24 hrs. yielded the monosubstituted product.

Anal. Calcd. for $Mn(CO)_4Sb(C_6H_5)_3Br$: C, 44.1; H, 2.50. Found: C, 43.7; H, 2.73.

At the conditions of the kinetic studies $Mn(CO)_3(C_6H_5NH_2)_2Br$[7,8] precipitated from the benzene solution. The precipitate was washed several times with benzene and dried.

Anal. Calcd. for $Mn(CO)_3(C_6H_5NH_2)_2Br$: C, 44.5; H, 3.46; N, 6.66. Found: C, 45.1; H, 3.47; N, 7.10.

The analogous toluidine compounds were obtained in the same manner.

Results

Kinetic data for reactions in chloroform solution are presented in Table I. The rate constants were evaluated from first order plots that are linear to 95% completion of reaction. Reactions of $Mn(CO)_5Cl$ and $Mn(CO)_5Br$ all went to completion. In the case of $Mn(CO)_5I$, equilibrium was attained after about 80% completion for all ligands. Consequently, Schropp's preparation of $Mn(CO)_4P(C_6H_5)_3I$ from equimolar quantities of $Mn(CO)_5I$ and $P(C_6H_5)_3$ was perhaps an equilibrium mixture.[3] In these reactions, formation of the disubstituted product, $Mn(CO)_3L_2X$, was not observed with $P(C_6H_5)_3$, $As(C_6H_5)_3$ and $Sb(C_6H_5)_3$ even after one month. However, $P(C_6H_5)Cl_2$, $P(OCH_2)_3CCH_3$, $P(OC_4H_9)_3$ and $P(OC_6H_5)_3$ continued to the disubstituted product within 24 hr. The nitrogen bearing ligands yielded the disubstituted product directly giving no evidence for a monosubstituted intermediate.

TABLE I

RATES OF REACTION OF $Mn(CO)_5X$ WITH VARIOUS REAGENTS IN CHLOROFORM

$$Mn(CO)_5X + L \longrightarrow Mn(CO)_4LX + CO$$

$Mn(CO)_5X$ (mole/l.)	Temp., °C.	Ligand, L	L (mole/l.)	10^5k, sec.$^{-1}$
		Rates for $Mn(CO)_5I$		
0.0190	29.9	$P(C_6H_5)_3$	0.240	0.348
.0171	35.1	$As(C_6H_5)_3$	.208	.824
.0175	35.1	$P(C_4H_9)_3$	.203	.844
.0199	39.2	$As(C_6H_5)_3$	.210	1.64
.0204	39.2	C_5H_5N	.240	1.79
		Rates for $Mn(CO)_5Br$		
0.0301	30.1	$P(C_6H_5)_3$	0.133	6.67
.0290	30.1	$P(C_6H_5)_3$	.344	6.78
.0299	30.1	$As(C_6H_5)_3$	.132	6.56
.0301	30.1	$As(C_6H_5)_3$	.387	6.59
.0297	30.1	$Sb(C_6H_5)_3$	.135	6.59
.0286	30.1	$Sb(C_6H_5)_3$	.353	6.65
.0226	40.2	$As(C_6H_5)_3$	.210	33.2
.0240	40.2	C_5H_5N	.258	33.0
.0230	47.8	$P(C_6H_5)_3$	.247	103
.0241	47.8	$As(C_6H_5)_3$	.206	101
		Rates for $Mn(CO)_5Cl$		
0.0135	21.8	$P(C_6H_5)_3$	0.258	16.7
.0158	21.8	$As(C_6H_5)_3$	.219	17.0
.0145	21.8	C_5H_5N	.242	18.0
.0199	30.2	$As(C_6H_5)_3$	.224	59.2
.0218	30.2	$P(OC_4H_9)_3$	.243	65.0
.0190	30.2	C_5H_5N	.232	61.6
.0188	40.0	$P(C_6H_5)_3$	.154	268
.0136	40.0	$As(C_6H_5)_3$	.105	258
.0136	40.2	$As(C_6H_5)_3$	.120	272

Table II gives the activation parameters calculated from the rate constants determined at three different temperatures. The rate constants for the reaction between $Mn(CO)_5Br$ and $As(C_6H_5)_3$ in a variety of solvents at 40° are collected in Table III. Also listed here are the dielectric constants of the different solvents at this temperature. It must be noted that $Mn(CO)_5Br$ decomposed in nitromethane and *o*-nitrotoluene at essentially the same rate as the above reaction in these solvents. In the absence of $As(C_6H_5)_3$, no new carbonyl product formed, although when $As(C_6H_5)_3$ was present, the desired product formed at the same rate as the disappearance of $Mn(CO)_5Br$. This

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(7) W. Hieber and W. Schropp, Jr., *Z. Naturforschg.*, **14b**, 460 (1959).

(8) T. H. Coffield and N. Hebert, U. S. Patent 2,902,489, Sept. 1, 1959.

same decomposition was noted in acetone also, but in this case a new carbonyl product was formed. In the absence of $As(C_6H_5)_3$, the reaction of $Mn(CO)_5Br$ with acetone produced ions and was readily followed by conductivity, but with $As(C_6H_5)_3$, the conductivity changed much more slowly, indicating the suppression of the $Mn(CO)_5Br$ reaction with acetone. Also the desired product was formed when $As(C_6H_5)_3$ was present, there being no infrared evidence for the $Mn(CO)_5Br$–acetone reaction product. The $Mn(CO)_5Br$–acetone product could not be converted to $Mn(CO)_4As(C_6H_5)_3Br$ by reaction with $As(C_6H_5)_3$. All attempts to isolate the $Mn(CO)_5Br$–acetone product have failed due to the apparent instability of the compound. 2-Butanone was also found to react with $Mn(CO)_5Br$, except that a good deal of decomposition accompanied the product formation. In 3-pentanone, the $Mn(CO)_5Br$ disappeared at essentially the same rate as in acetone, but in this case there was no evidence for a CO containing product. In the less polar solvents the very slow formation of $[Mn(CO)_4Br]_2$[2] was noted but was too slow to affect the reaction under investigation.

TABLE II

ACTIVATION PARAMETERS FOR THE REACTION OF $Mn(CO)_5X$ WITH $As(C_6H_5)_3$ IN CHLOROFORM

	E_a (kcal./mole)	ΔS^* (e.u.)
$Mn(CO)_5Cl$	27.5 ± 0.4	15.7
$Mn(CO)_5Br$	29.8 ± .4	18.9
$Mn(CO)_5I$	32.2 ± .4	20.7

TABLE III

RATES OF REACTION OF $Mn(CO)_5Br$ WITH $As(C_6H_5)_3$ IN A VARIETY OF SOLVENTS AT 40.0°

Solvent	Dielectric constant[a]	10^4k, sec.$^{-1}$
Cyclohexane	1.99	7.44
Carbon tetrachloride	2.20	5.45
Carbon disulfide	2.59	4.68
Toluene	2.34	4.54
Benzene	2.24	4.08
Chloroform	3.73	3.29
Chlorobenzene	4.65	3.24
2-Butanone	17.4	1.83
Acetone	19.6	1.79
o-Nitrotoluene	24.4	1.20
Nitromethane	34.8	1.17
Nitrobenzene[b]	33.7	1.08

[a] Dielectric constants from National Bureau of Standards, Circular 514. [b] Rate constant for $Mn(CO)_5Cl$ is 9.37×10^{-4} sec.$^{-1}$.

Table IV gives rate constants for the reaction of $Mn(CO)_5Br$ with $As(C_6H_5)_3$ in nitrobenzene at several temperatures. Table V summarizes the rate constants for the reactions of $Mn(CO)_5Br$ with ligands which manifest specific solvent effects. The infrared spectra in the carbonyl stretching region of some of the reaction products are shown in Table VI.

TABLE IV

RATES OF REACTION OF $Mn(CO)_5Br$ WITH $As(C_6H_5)_3$ IN NITROBENZENE

$Mn(CO)_5Br$ (mole/l.)	Temp., °C.	$As(C_6H_5)_3$ (mole/l.)	10^4k, sec.$^{-1}$
0.0121	30.0	0.0997	1.98
.0114	40.0	.0919	10.7
.0115	40.0	.0994	10.8
.0169	48.0	.103	34.9
.0124	48.0	.166	36.4

TABLE V

RATES OF REACTION OF $Mn(CO)_5Br$ WITH LIGANDS THAT ALTER THE RATE (40°)

Complex (mole/l.)	Ligand	Ligand (mole/l.)	10^4k, sec.$^{-1}$	Solvent
0.0112	$P(C_6H_5)Cl_2$	0.221	2.46	Benzene
.0118	$P(C_6H_5)Cl_2$	.442	2.62	Benzene
.0125	$P(C_6H_5)Cl_2$	.295	0.874	Nitrobenzene
.0117	C_2H_5NC	.311	2.22	Chlorobenzene
.0124	C_2H_5NC	.487	1.93	Chlorobenzene
.0116	C_2H_5NC	1.35	2.25	Chlorobenzene
.0112	$C_6H_5NH_2$	0.220	3.31	Benzene
.0113	$C_6H_5NH_2$	1.10	3.36	Benzene
.0107	*p*-$H_3CC_6H_4NH_2$	0.218	3.98	Benzene
.0112	*o*-$H_3CC_6H_4NH_2$	0.187	2.74	Benzene
.0145	*o*-$ClC_6H_4NH_2$	1.33	2.69	Benzene
.00129	$P(OC_6H_5)_3$	0.0764	3.04	Chloroform
.00157	$P(OCH_2)_3CCH_3$	0.0292	2.56	Chloroform

TABLE VI

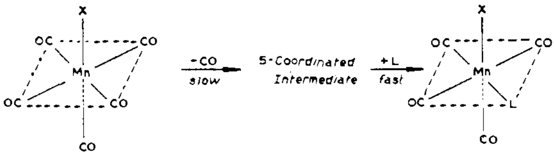
INFRARED CARBONYL ABSORPTIONS OF REACTION PRODUCTS IN CHLOROFORM

Compound	Cm.$^{-1}$[a]
$Mn(CO)_4[P(C_6H_5)Cl_2]Br$	2114, 2032, 1988
$Mn(CO)_4[P(OCH_2)_3CCH_3]Br$	2110, 2032, 1980
$Mn(CO)_4[P(OC_6H_5)_3]Br$	2101, 2020, 1972
$Mn(CO)_4[P(OC_4H_9)_3]Br$	2105, 2016, 1972
$Mn(CO)_4[P(C_6H_5)_3]Br$	2101, 2012, 1965
$Mn(CO)_4[As(C_6H_5)_3]Br$	2097, 2016, 1965
$Mn(CO)_4[Sb(C_6H_5)_3]Br$	2092, 2016, 1965
$Mn(CO)_4[P(C_6H_5)_3]Cl$	2101, 2016, 1965
$Mn(CO)_4[As(C_6H_5)_3]Cl$	2101, 2020, 1961
$Mn(CO)_4[As(C_6H_5)_3]I$	2092, 2016, 1965
$Mn(CO)_4[P(C_6H_5)_3]I$	2088, 2016, 1953
$Mn(CO)_4[P(C_4H_9)_3]Br$	2083, 2004, 1949
$Mn(CO)_3[P(C_6H_5)Cl_2]_2Br$	2058, 2004, 1953
$Mn(CO)_3[P(OCH_2)_3CCH_3]_2Br$	2066, 2012, 1957
$Mn(CO)_3[P(OC_6H_5)_3]_2Br$	2053, 2000, 1949
$Mn(CO)_3[P(OC_4H_9)_3]_2Br$	2037, 1969, 1927
$Mn(CO)_3[P(C_4H_9)_3]_2I$	2016, 1946, 1894
$Mn(CO)_3(C_6H_5NH_2)_2Br$	2037, 1938, 1905[b]
$Mn(CO)_3(o\text{-}CH_3C_6H_4NH_2)_2Br$	2037, 1942, 1905[b]
$Mn(CO)_3(p\text{-}CH_3C_6H_4NH_2)_2Br$	2037, 1942, 1905[b]

[a] ± 5 cm.$^{-1}$. The relative intensities of the absorptions at each wave number in the order given in the Table are: $Mn(CO)_4LX$ – (m), (s), (s) and $M(CO)_3L_2X$ – (s)(s)(s). [b] Using KBr disk.

Discussion

The results of this investigation show that reaction 1 occurs at moderate conditions to produce monosubstituted products of the type $Mn(CO)_4LX$. Furthermore the kinetic data in Table I demonstrate that the rate of substitution is not dependent on L. This suggests that the rate determining step is the dissociation of carbon monoxide from $Mn(CO)_5X$ followed by the rapid entry of L (2).



(2)

Such a process accounts for the experimental observations and is also in accord with the mechanism proposed for the exchange of carbon monoxide with the four more labile CO's in $Mn(CO)_5X$. Since both the exchange and reactions with L are believed to be involved in the same initial slow step, it follows that the rates of these should be the same. In agreement with this is the observation that $Mn(CO)_5Br$ in toluene at 31.8° reacts with $P(C_6H_5)_3$ or C_5H_5N with a rate constant of 1.3×10^{-4} sec.$^{-1}$ compared to the value of 1.2×10^{-4} sec.$^{-1}$ reported for CO exchange at these conditions.

The structures of the monosubstituted products are not known but are presumed to be that shown in equation 2. This structure is chosen on the basis of the current view that the M–C bond strength in metal carbonyls is in part due to *dp*-π bonding resulting from the delocalization of *d*-orbital electrons of the metal into vacated *p*-orbitals of carbon, *e.g.* M=C=O. Because of the geometry of the *d* orbitals, ligands in *trans* positions compete for the same sets of orbitals. Since the π-bonding tendency of CO exceeds that of X, it follows that the CO *trans* to X should have a greater degree of Mn–C multiple bonding than do the four CO's in the plane opposite each other. That the M–C bond strength of one CO, presumably that *trans* to X, is greater than it is for the other four is in agreement with the observation that one CO exchanges much less readily than do the other four. The fact that the four labile CO's exchange at the same rate as their replacement by L further supports the *cis* structure. The configuration of the five coördinated intermediate is not known; it could quite possibly be either a tetragonal pyramid, a trigonal bipyramid or a structure intermediate between these two.

The data in Table I show that the rate of reaction of $Mn(CO)_5X$ decreases with changes in X in the order Cl > Br > I. This reactivity order has been explained on the basis of the polarizability (or electronegativity) of the halide ions. Briefly this explanation suggests that the more polarizable (or less electronegative) iodide ion results in a greater electron density on manganese which in turn means a greater back-donation of d-orbital electrons, a greater Mn–C bond strength and thus a slower reaction. This is in accord with the increasing CO stretching frequency of the more intense band at the higher frequency, presumably that of the four CO's in a plane, for $Mn(CO)_5X$ as the atomic number of X decreases, *e.g.* I, 2056; Br, 2064; Cl, 2070 cm.$^{-1}$. The order of decreasing Mn=C=O bonding is indicated. Thus the activation energies (Table II) are related to the strength of this bond, but also one must not ignore the difference in energies of the activated complex for the three halides. This may be of great importance although it cannot be accurately evaluated at the present time.

Also shown in this table are the entropies of activation, all of which are positive. This is to be expected for a dissociation process where the transition state is less restricted than the ground state because of the increased Mn–C bond length. The positive entropy shows a small but progressive increase in the order Cl<Br<I. If it is assumed that the transition state is less solvated than the ground state, resulting in an increase in entropy, then the results may be explained on the basis that this difference in solvation is largest for the iodo system. This suggests that the polarity of the activated complex is less than that of the parent compound and that $Mn(CO)_5I$ shows the maximum difference in polarity.

Support is given to the decrease in polarity accompanying these reactions by the data in Table III. These show that for a particular reaction, the rate decreases with an increase in polarity of the solvent. To further substantiate this effect, an activation energy of 30.9 kcal./mole in nitrobenzene was calculated from the data in Table IV. Since the two standard deviation limits of accuracy for activation energies in chloroform and nitrobenzene nearly overlap, a statistical treatment was used. A standard deviation calculated from the rates in chloroform at 30.1° was applied to the rates at all temperatures in both solvents. Such a treatment of the rates in chloroform and nitrobenzene gave $[(Ea)_{C_6H_5NO_2} - (Ea)_{CHCl_3}] = 1.7$ kcal./mole with 95% confidence limits of ±0.7 kcal./mole. This then gives $[(\Delta S^{\ddagger})_{C_6H_5NO_2} - (\Delta S^{\ddagger})_{CHCl_3}] = 3.2 \pm 2.1$ e.u. The higher activation energy in nitrobenzene can be interpreted as a greater loss in solvent stabilization as the $Mn(CO)_5Br$ proceeds to the less polar activated complex. It is interesting that the solvent stabilization of $Mn(CO)_5Br$ is an enthalpy effect, whereas the entropy term favors the less polar activated complex in nitrobenzene over that in chloroform. A simple electrostatic picture predicts that the faster rates in the less polar solvents are due to a larger entropy of activation, the enthalpy term being relatively insignificant.[9] This suggests that specific solvent effects may be more important than the dielectric strengths, but in view of the smallness of the effects, more definite interpretation is not possible.

One question remains unanswered and that is why should this difference in polarity between $Mn(CO)_5X$ and the activated complex reach a maximum with $Mn(CO)_5I$? It was found that the ratio of rates of reaction in nitrobenzene to that in chloroform is larger for $Mn(CO)_5Cl$ than for $Mn(CO)_5Br$. This too indicates that the relative decrease in polarity in going from $Mn(CO)_5X$ to the activated complex is greater for the bromo compound than for the chloro compound. One possible explanation for this relative decrease in polarity is that the Mn-X bond length in the transition state is shorter than in the ground state. Further decrease in polarity can be attributed to the greater polarization of the more polarizable halides at this shorter bond distance. This effect should be greater for the large polarizable iodide ion than for the chloride ion.

The results in Table V show that the rates of reaction of $Mn(CO)_5Br$ with certain ligands are slower than the reaction with $As(C_6H_5)_3$ at the same conditions (Table III). However, the rates of reaction for these ligands also do not depend upon their concentration. That the rates are slower is perhaps due to specific solvent effects. It is interesting that this effect is larger in the less polar

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[9] A. A. Frost and R. G. Pearson, "Kinetics and Mechanisms," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 126.

benzene than in the more polar nitrobenzene. Similar solvent effects were also found in some phosphine exchanges of nickel-carbonyl-phosphine complexes.[10]

The extent of reaction 1 in these systems seems to depend more on the base strength of the entering ligand than on its ability to π-bond. For example the reaction of $Mn(CO)_5Br$ with $P(C_6H_5)Cl_2$ goes to completion but PCl_3 does not react. This is the order of decreasing base strength but increasing π-bonding tendency for the phosphorus compounds.[11]

Likewise aniline, *o*- and *p*-toluidine which are not expected to π-bond significantly react completely. No reaction was observed for *p*-nitroaniline. Not only does there appear to be a lower limit of basicity below which this reaction does not take place at these conditions but also an upper limit above which a different reaction occurs. Stronger bases such as cyclohexylamine, dimethylamine and diethylamine react very rapidly with $Mn(CO)_5X$ to displace X^- rather than CO. No further study has as yet been made of this reaction.

The infrared spectra of some $Mn(CO)_4LX$ compounds in the C–O stretching region are similar but show an increase in wave number of absorption with changes in L in the order

$$P(C_4H_9)_3 < P(C_6H_5)_3 \sim As(C_6H_5)_3 \sim Sb(C_6H_5)_3 < P(OC_4H_9)_3 \leqslant P(OC_6H_5)_3 < P(OCH_2)_3CCH_3 \leqslant P(C_6H_5)Cl_2$$

This same order has been found in the tetrahedral nickel–carbonyl–phosphine complexes[10,12] and has been correlated with the π-bonding ability of the phosphine, the best π-bonding phosphines yielding complexes with the highest carbonyl absorption frequencies.

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[CONTRIBUTION FROM THE RESEARCH CENTER, HERCULES POWDER COMPANY, WILMINGTON 99, DELAWARE]

Acylcobalt Carbonyls and their Triphenylphosphine Complexes[1]

BY RICHARD F. HECK AND DAVID S. BRESLOW

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A number of acylcobalt tetracarbonyls have been prepared by reaction of sodium cobalt tetracarbonyl with acyl halides or with alkyl halides and CO. The properties of these unstable compounds are described. Acylcobalt tricarbonyl triphenylphosphines have been prepared from acylcobalt tetracarbonyls and triphenylphosphine or in one step from alkyl halides, sodium cobalt tetracarbonyl and triphenylphosphine. These relatively stable, crystalline, high-melting derivatives have been isolated and characterized. Several unusual reactions of acylcobalt complexes containing functional groups have been described.

Introduction

Three methods have been reported for the synthesis of acylcobalt tetracarbonyls, $RCOCo(CO)_4$: reaction of an acyl halide with cobalt tetracarbonyl anion, reaction of an alkyl halide with cobalt tetracarbonyl anion and CO, and the addition of cobalt hydrocarbonyl and CO to an olefin.[2–6] The purpose of this work was to study in greater detail the preparation and properties of simple acylcobalt compounds, the effect of various functional groups on their chemistry and the preparation of stable triphenylphosphine adducts.

Discussion

The acyl halide procedure is the most generally useful one for the preparation of acylcobalt tetracarbonyls. Yields are generally high, providing the reactions are carried out in dilute solution at low temperatures with acid-free acyl halides under anhydrous conditions.[7,8] The alkylation of sodium cobalt tetracarbonyl in the presence of CO is a less useful procedure, operating well only with active alkylating agents, such as methyl

[1] A preliminary account of a portion of this work appeared in *J. Am. Chem. Soc.*, **82**, 4438 (1960).

[2] D. S. Breslow and R. F. Heck, *Chem. & Ind. (London)*, 467 (1960).

[3] R. F. Heck and D. S. Breslow, *Actes du Deuxième Congrès International de Catalyse*, Vol. I, Editions Technip, Paris, 1960, p. 671.

[4] R. F. Heck and D. S. Breslow, *J. Am. Chem. Soc.*, **83**, 1097 (1961).

[5] R. F. Heck and D. S. Breslow, "Advances in the Chemistry of the Coördination Compounds," edited by S. Kirschner, Macmillan Co., New York, N. Y., 1961, p. 281.

[6] R. F. Heck and D. S. Breslow, *J. Am. Chem. Soc.*, **83**, 4023 (1961).

[7] Free acid reacts with sodium cobalt tetracarbonyl to form hydrocarbonyl, which is known to reduce acylcobalt carbonyls to aldehydes.[2,3,6]

[8] Trifluoroacetic anhydride yielded trifluoroacetylcobalt tetracarbonyl as an unusually stable acylcobalt compound in agreement with the recent report of Hieber, Beck and Lindner.[9] McClellan[10] reported that perfluoroacylcobalt tetracarbonyls lose CO spontaneously below 0° and cannot be isolated. Inasmuch as McClellan used perfluoroacyl halides instead of the anhydrides, it would appear that in these cases traces of either hydrogen halide or perfluorocarboxylic acid catalyze the elimination of CO to give perfluoroalkylcobalt tetracarbonyls.

[9] W. Hieber, W. Beck and E. Lindner, *Z. Naturforsch.*, **16b**, 229 (1961).

[10] W. R. McClellan, *J. Am. Chem. Soc.*, **83**, 1598 (1961).