Metal Carbonyls. VI. Isomerism of Disubstituted Manganese Pentacarbonyl Bromide

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cis- and trans-Mn(CO)₃[P(OC₆H₅)₃]₂Br have been prepared and identified by their dipole moments and infrared spectra. Analogous isomers of Mn(CO)₃L₂Br, where L = P(C₆H₅)Cl₂, P(OC₄H₉)₃ and P(C₄H₉)₃, have also been prepared (C₄H₉ is always n-butyl). The cis isomer, obtained from the reaction of Mn(CO)₅Br with L, isomerizes to the trans form in solution and the extent of isomerization increases with increase in size of L. The results of a kinetic study suggest an intermolecular mechanism of isomerization involving the dissociation of L.

Disubstituted compounds of the manganese pentacarbonyl halides were first prepared by the reaction between Mn(CO)₅X (where X⁻ = Cl⁻, Br⁻ or I⁻) and the desired ligand, L, at 120° in the absence of solvent.[1] The products, Mn(CO)₃L₂X, where L = P(C₆H₅)₃, As(C₆H₅)₃ or C₅H₅N, were assigned a structure in which the L's were cis to each other as well as to X.

The present study reports the preparation, from organic solvents, of these and other compounds. The compounds obtained were found to exist in two isomeric forms, the relative stabilities of which depend upon L. The kinetics and mechanism of isomerization were also investigated.

Experimental

Preparation and Purification of Materials.—The starting material, Mn(CO)₅Br, was prepared as described.[1] The preparation and purification of the ligands and solvents were previously reported.[2,3]

cis-Mn(CO)₃[P(OC₆H₅)₃]₂Br, in which the triphenyl phosphite groups are cis to each other as well as to Br, was prepared by the reaction of 1.1 g. of P(OC₆H₅)₃ with 0.2 g. of Mn(CO)₅Br in approximately 15 ml. of chloroform at 37° for 12 hr. At the end of this time 30 ml. of n-hexane was added, and the resulting solution was evaporated to approximately 5 ml. under a stream of nitrogen. The yellow crystals obtained were collected on a filter, dissolved in 2 ml. of chloroform and precipitated with 30 ml. of hexane. The precipitate was washed with hexane and allowed to dry at room temperature.

Anal. Calcd. for Mn(CO)₃[P(OC₆H₅)₃]₂Br: C, 55.7; H, 3.58. Found: C, 55.2; H, 3.74.

trans-Mn(CO)₃[P(OC₆H₅)₃]₂Br, in which the triphenyl phosphite groups are trans to each other but cis to Br, was prepared in the same manner except that the reaction was carried out at 55–60° for 16 hr. It was purified as above.

Anal. Found: C, 55.1; H, 3.56.

Analogous isomers of Mn(CO)₃[P(C₆H₅)Cl₂]₂Br, Mn(CO)₃[P(C₄H₉)₃]₂Br and Mn(CO)₃[P(OC₄H₉)₃]₂Br, prepared in the same manner, were not isolated but identified only by their infrared spectra which were very similar to those of the established Mn(CO)₃[P(OC₆H₅)₃]₂Br isomers.

Dipole Moment Determinations.—The dipole moments of cis- and trans-Mn(CO)₃[P(OC₆H₅)₃]₂Br and Mn(CO)₅Br were determined by the approximate method of Jensen,[4] using only dielectric constant measurements. The necessary capacitance measurements were made on 0.015 to 0.035 M benzene solutions of the complexes with a General Radio Co. capacitance measuring assembly, type no. 1610-A, set at 1000 cycles per second. The average deviation of the dipole moments calculated from these data was less than 3%.

Molecular Weight Determination.—The molecular weight of trans-Mn(CO)₃[P(OC₆H₅)₃]₂Br was determined in benzene by the method of freezing point depression. A solution of 0.5102 g. of the complex in 15 ml. of benzene gave a 0.260° freezing point depression, indicating a molecular weight of 761.

Ultraviolet Spectra.—The spectra of the isomers were taken with a Beckman DK2 double beam recording spectrophotometer adjusted for maximum resolution. Corresponding spectra of the isomers were taken on the same paper with identical instrumental settings to minimize mechanical errors.

Determination of Rates of Isomerization.—The rates of cis → trans isomerization were determined by following the disappearance of the highest frequency carbonyl absorption of the cis isomer. A Baird Associates Model 4–55 double beam recording spectrophotometer with NaCl optics was used to follow the

reaction as well as to determine the absorptions of the cis and trans isomers. A polystyrene standard was used for calibration.

For rate studies of the isomerization of cis-Mn(CO)₃[P(OC₆H₅)₃]₂Br, the solid complex was dissolved in the desired solvent and its rate of isomerization was followed. However, the reaction solutions of cis-Mn(CO)₃L₂Br, where L = P(C₆H₅)Cl₂, P(C₄H₉)₃ or P(OC₄H₀)₃, were prepared by allowing an excess of L to react with Mn(CO)₅Br in 3 ml. of sym-tetrachloroethane (TCE) at 38° for 12 to 20 hr. These solutions were then diluted to 20 ml., placed in aluminum foil-wrapped flasks, and thermostated in a constant temperature bath. Approximately 5 min. was allowed for the system to attain equilibrium temperature before a sample was withdrawn with a syringe and placed in an infrared cell. Typical changes in spectra with time are shown in Fig. 1. The spectrum at $t = 0$ min. is that of cis-Mn(CO)₃[P(OC₆H₅)₃]₂Br, while that at $t = \infty$ is trans-Mn(CO)₃[P(OC₆H₅)₃]Br. First-order rate constants were obtained from the slopes of plots of ln $(A - A_\infty)$ vs. t, time, where A is the absorbance at time t. In all cases A_∞ was zero. All isomerizations continued to completion and gave linear plots to at least 80% completion, except for cis-Mn(CO)₃[P(C₆H₅)Cl₂]₂Br for which significant deviations began to appear after 50% completion. The explanation for such a behavior is unknown.

Results

The cis and trans isomers of Mn(CO)₃[P(OC₆H₅)₃]₂Br were prepared and identified by their dipole moments (Table I), near-ultraviolet spectra and infrared spectra (Fig. 1 and Table II). The cis-Mn(CO)₃L₂Br compounds isomerize to the trans isomers at rates which depend upon L in the complex and upon the solvent (Table III). The P(OC₆H₅)₃ groups in cis-Mn(CO)₃[P(OC₆H₅)₃]₂Br are displaced by P(OC₄H₉)₃ and P(C₆H₅)₃ at a rate which is independent of the concentration and nature of the entering ligand and which is much faster than the rate of isomerization under the same conditions (Table IV).

TABLE I

DIPOLE MOMENTS OF Mn(CO)₃L₂Br ISOMERS

Compound	μ, Debyes
cis-Mn(CO)₃[P(OC₆H₅)₃]₂Br	4.78
trans-Mn(CO)₃[P(OC₆H₅)₃]₂Br	3.53
Mn(CO)₅Br	3.39[a]

[a] This value compares with 3.19 ± 0.03 D. obtained by a more accurate method by Beck, et al.[5]

TABLE II

INFRARED SPECTRA OF cis- AND trans-Mn(CO)₃L₂Br IN TCE

L	cis (s)	(s)	(s)	trans (w)	(vs)	(s)
P(C₆H₅)Cl₂	2058	2004	1953	2075	2004	1953
P(OC₆H₅)₃	2053	2000	1949	2070	2000	1949
P(OC₄H₉)₃	2037	1969	1927	2049	1969	1927
P(C₄H₉)₃	2008	1938	1894	2020	1938	1894[a]

[a] Measured in P(C₄H₉)₃ solvent.

Discussion

Identification of Isomers.—A compound of the composition Mn(CO)₃[P(OC₆H₅)₃]₂Br was prepared by the reaction of Mn(CO)₅Br with P(OC₆H₅)₃ at 37°. A solution of this compound when heated to 55° yields a product having a different infrared spectrum but the same composition. During this reaction there is no evolution of carbon monoxide, which suggests

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

(2) R. J. Angelici and F. Basolo, *J. Am. Chem. Soc.*, **84**, 2495 (1962).

(3) R. J. Angelici and F. Basolo, *Inorg. Chem.*, **2**, 728 (1963).

(4) K. A. Jensen, *Acta Chem. Scand.*, **3**, 479 (1949).

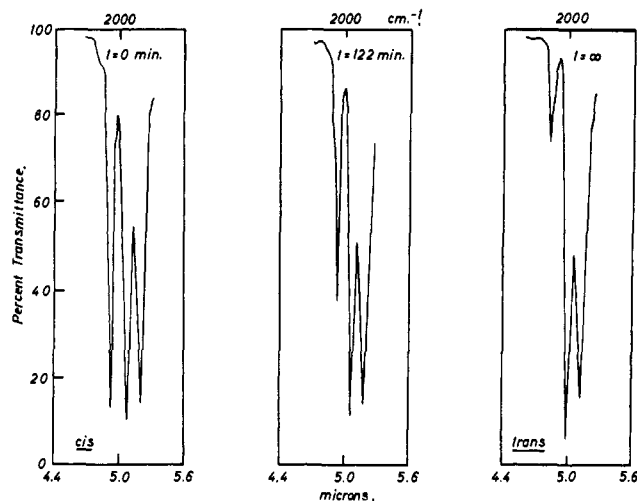(5) W. Beck, W. Hieber and H. Tengler, *Chem. Ber.*, **94**, 862 (1961).

Fig. 1.—Infrared spectra during the isomerization of cis-Mn(CO)₃[P(OC₆H₅)₃]₂Br in the presence of excess P(OC₆H₅)₃ in TCE at 60.1°.

TABLE III
RATES OF ISOMERIZATION OF cis-Mn(CO)₃L₂Br IN TCE IN THE PRESENCE OF EXCESS L

L in complex	10^3[complex], M	Added L, M	T, °C.	10^5k, sec.$^{-1}$
P(C₆H₅)Cl₂	7.11	0.209	42.0	3.08
P(C₆H₅)Cl₂	6.91	.539	42.0	3.05
P(C₆H₅)Cl₂	5.77	.171	50.2	9.76
P(C₆H₅)Cl₂	5.83	.171	50.2	10.2
P(C₆H₅)Cl₂	6.87	.436	50.2	10.3
P(C₆H₅)Cl₂	7.69	.206	60.1	29.6
P(C₆H₅)Cl₂	7.69	.206	60.1	30.2
P(C₆H₅)Cl₂	7.64	.539	60.1	29.9
P(OC₆H₅)₃	4.80	.0	50.2	4.19
P(OC₆H₅)₃	4.14	.0	50.2	4.15
P(OC₆H₅)₃	4.68	.0	60.1	16.6
P(OC₆H₅)₃	4.84	.0	60.1	17.7[a]
P(OC₆H₅)₃	5.84	.0	60.1	21.0[b]
P(OC₆H₅)₃	5.80	.0	60.1	21.9[c]
P(OC₆H₅)₃	5.95	.0	70.0	56.7
P(OC₆H₅)₃	52.0	.0	70.0	46.7
P(OC₆H₅)₃	4.68	.0153	50.2	2.29
P(OC₆H₅)₃	4.70	.0764	50.2	2.28
P(OC₆H₅)₃	5.98	.00116	60.1	10.9
P(OC₆H₅)₃	5.80	.00274	60.1	10.8
P(OC₆H₅)₃	5.99	.00802	60.1	9.89
P(OC₆H₅)₃	6.18	.0190	60.1	9.65
P(OC₆H₅)₃	5.76	.0956	60.1	9.74
P(OC₆H₅)₃	5.70	.0190	70.0	35.1
P(OC₆H₅)₃	6.00	.0956	70.0	34.5
P(OC₄H₉)₃	5.77	.0628	50.2	0.785
P(OC₄H₉)₃	5.86	.156	50.2	0.776
P(OC₄H₉)₃	6.07	.0688	60.1	3.45
P(OC₄H₉)₃	6.15	.150	60.1	3.53
P(OC₄H₉)₃	7.34	.0783	70.0	13.5
P(OC₄H₉)₃	7.59	.185	70.0	13.6
P(C₄H₉)₃	58.9	. . .	50.2	2.06[d]
P(C₄H₉)₃	47.4	. . .	70.0	24.7[d]

[a] Dielectric constant (20°) of TCE is 8.2.   [b] Toluene solvent; dielectric constant (20°) is 2.4.   [c] Nitrobenzene solvent; dielectric constant (20°) is 35.2.   [d] Measured in P(C₄H₉)₃ solvent.

that no polymerization has occurred. In addition, the product has an experimentally determined molecular weight of 761 which compares with 839 calculated for the monomeric compound. The differences between these compounds must, therefore, lie in the relative positions of the groups in the coördination sphere.

The compound prepared at 37° has been assigned[6] a structure in which the P(OC₆H₅)₃ groups are cis to

TABLE IV
RATES OF REACTION OF Mn(CO)₃[P(OC₆H₅)₃]₂Br WITH L AT 60.1° IN TCE

Isomer	$10^3 M$	Reagent L	[L], M	10^4k, sec.$^{-1}$
cis	5.20	P(C₆H₅)₃	0.0406	1.4[a]
cis	4.92	P(C₆H₅)₃	.0790	1.4[a]
cis	4.86	P(C₆H₅)₃	.0385	5.8[b]
cis	5.58	P(C₆H₅)₃	.0776	6.6[b]
cis	4.67	P(C₆H₅)₃	.0207	19
cis	5.26	P(C₆H₅)₃	.0464	22
cis	5.06	P(C₆H₅)₃	.0796	21
cis	5.56	P(OC₄H₉)₃	.0506	∼20[c]
trans	4.07	P(C₆H₅)₃	.0419	3.4[c]
trans	4.18	P(OC₄H₉)₃	.0504	2.7[c]

[a] Measured at 40.0°.   [b] Measured at 50.0°.   [c] Rate difficult to measure because of overlapping bands in the infrared spectrum.

the Br as well as to each other; this isomer is designated cis-Mn(CO)₃[P(OC₆H₅)₃]₂Br. The product of the isomerization (1) at 55° is trans-Mn(CO)₃[P(OC₆H₅)₃]₂Br, in which the P(OC₆H₅)₃ groups are trans

(1)
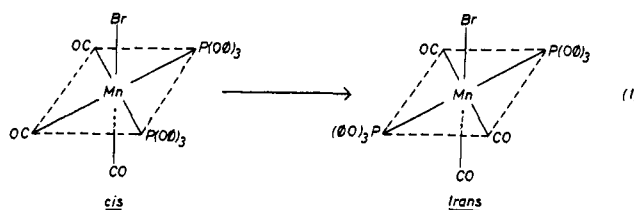
cis   trans

to each other but cis to Br. The following observations support these assignments.

A dipole moment study yielded the results shown in Table I. As expected, the trans isomer has a dipole moment close to that of the unsubstituted Mn(CO)₅Br. However, the higher moment of the second isomer does not distinguish between the cis isomer and the other possible isomer, in which the P(OC₆H₅)₃ groups are cis to each other but one is trans to Br.

The infrared spectrum of the cis isomer has absorption bands in the carbonyl stretching region at 2053(s), 2000(s) and 1949(s) cm.$^{-1}$, compared with 2070(w), 2000(vs) and 1949(s) for the trans isomer. These spectra are shown in Fig. 1.

The trans compound has C₂ᵥ symmetry which gives rise to three carbonyl stretching absorptions (2A₁ + B₁) as observed. The normal modes of vibration having these symmetries are shown in Fig. 2. The A₁ᵇ mode does not involve a change in dipole moment but is observed because of coupling with the A₁ᵃ mode or because of distortion of the molecule from C₂ᵥ symmetry.[7] Hence the symmetrical stretching mode A₁ᵇ) should result in a weak absorption as observed in the spectrum. Thus the infrared spectrum confirms the trans isomer assignment previously made on the basis of dipole moment determinations. The A₁ᵃ mode is assigned to the band at lowest frequency, since the CO trans to Br is expected to have the greatest degree of Mn=CO π-bonding. It is interesting that both the position and intensity of this absorption are the same in the cis isomer. The total intensity of the bands (A₁ᵇ + B₁) of the trans-CO's is roughly twice that of the single CO trans to the bromide, as expected from very elementary arguments.[7]

The Cₛ symmetry of the cis isomer leads to three expected absorption bands (2A′ + A″). All modes (Fig. 2) involve dipole changes and hence none should give weak absorptions. The other possible isomer, where one P(OC₆H₅)₃ group is trans to Br, would be

(6) R. J. Angelici, F. Basolo and A. J. Poë, Nature, 195, 993 (1962).

(7) L. E. Orgel, Inorg. Chem., 1, 25 (1962).

expected to yield a spectrum with a weak absorption. The observed spectrum containing three strong bands strongly supports the *cis* assignment to this isomer. As mentioned above, the lowest frequency band is that of the A_b' mode; the remaining two bands then arise from the symmetric and asymmetric stretching vibrations of the two equivalent *cis* CO's. The total intensity of the absorptions of the two CO's *cis* to Br is approximately twice that of the CO *trans* to Br.

It is also known that the CO *trans* to the bromide is more inert than those *cis* to the bromide in $Mn(CO)_5$-Br,[8] and monosubstitution occurs in the *cis* position.[2,3] It therefore seems reasonable from chemical evidence that substitution *cis* to Br will occur in the monosubstituted compounds as well. Furthermore, current π-bonding theories suggest that a CO *trans* to another CO is more readily replaced than CO *trans* to some lesser π-bonding ligand. Thus the chemical evidence is generally very much in favor of these *cis*- and *trans*-$Mn(CO)_3[P(OC_6H_5)_3]_2Br$ assignments.

The near-ultraviolet spectra of the *cis*-$Mn(CO)_3$-$[P(OC_6H_5)_3]_2Br$ in TCE has its absorption maximum at 385 mμ with ϵ 810 l./mole cm., while the *trans* compound absorbs at 398 mμ with ϵ 720. The absorption of the *cis* isomer is more symmetric about the maximum than the *trans* isomer absorption. This is reasonable since the *cis* isomer has a tetragonal ligand field, and therefore the more unsymmetrical rhombic field of the *trans* compound is expected to result in a greater number of transitions. In the ultraviolet region, both isomers have an absorption maximum at 283 mμ with ϵ 1100 l./mole cm. for the *cis* and ϵ 1200 for the *trans*.

Analogous *cis*- and *trans*-$Mn(CO)_3L_2Br$ isomers were prepared *in situ* for L = $P(OC_4H_9)_3$, $P(C_4H_9)_3$ and $P(C_6H_5)Cl_2$. These were identified by their infrared spectra (Table II), which have the same form as those of the isomers of $Mn(CO)_3[P(OC_6H_5)_3]_2Br$. The preparation of *trans*-$Mn(CO)_3[P(C_4H_9)_3]_2Br$ could only be accomplished in $P(C_4H_9)_3$ as the solvent because of decomposition in TCE when converting the *cis* compound to the *trans* form at higher temperatures.

Attempts to prepare *cis*-$Mn(CO)_3[P(C_6H_5)_3]_2Br$ were not successful. When a TCE solution containing a mixture of $Mn(CO)_5Br$ and $P(C_6H_5)_3$ is kept at 37° for two days, only $Mn(CO)_4P(C_6H_5)_3Br$ results.[2] However, if the temperature is raised to 55°, then a reaction begins to take place yielding a compound having an infrared spectrum very similar to *trans*-$Mn(CO)_3[P(OC_6H_5)_3]_2Br$. The reaction of $Mn(CO)_5$-Br and $P(C_6H_5)_3$ in the absence of solvent at 120° gives $Mn(CO)_3[P(C_6H_5)_3]_2Br$, as was reported previously by Abel and Wilkinson.[1] Their reported frequencies were reproduced on this compound. However, the band intensities again correspond to the *trans* structure rather than to the *cis* structure originally proposed. The earlier *cis* assignment was based on the similarity of the infrared absorptions of the $Mn(CO)_3L_2Br$ compounds and $Mn(CO)_3(bipy)Br$, for which the structure must be *cis*. The reaction of $Mn(CO)_5Br$ and pyridine in solution of 37° gives *cis*-$Mn(CO)_3(py)_2Br$ as shown by its three almost equally intense infrared absorptions. Upon heating to 60° no rearrangement to the *trans* structure occurs, as noted from the spectrum. Hence Abel and Wilkinson's $Mn(CO)_3(py)_2Br$ structural assignment is correct. *cis*-$Mn(CO)_3(C_6H_5NH_2)_2Br^2$ behaves like the similar pyridine compound. Like *trans*-$Mn(CO)_3[P(C_6H_5)_3]_2Br$, the analogous $As(C_6H_5)_3$ and $Sb(C_6H_5)_3$ compounds are probably also *trans*, since the disubstituted products do not form at the lower temperature (37°) used for the preparation of the *cis* isomers.

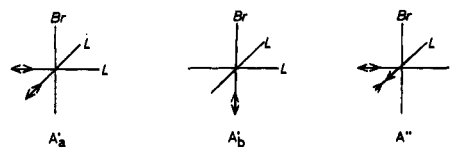(8) A. Wojcicki and F. Basolo, *J. Am. Chem. Soc.*, **83**, 525 (1961).
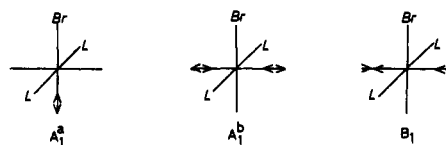
Fig. 2.—Normal modes of C–O stretching vibrations for isomers of $Mn(CO)_3L_2Br$.

It is noteworthy that it is not possible to construct the sterically crowded *cis*-$Mn(CO)_3[P(C_6H_5)_3]_2Br$ compound with Fisher–Taylor–Hirschfelder models, whereas the *trans* isomer is quite easily assembled. It can also be seen from models that $P(C_6H_5)_3$ is considerably more bulky than those ligands which form *cis* isomers.

When a chloroform solution of *cis*-$Mn(CO)_3[P-(OCH_2)_3CCH_3]_2Br^{2,3}$ is kept at 50° for 24 hours, it attains equilibrium containing only 20% of the *trans* isomer. This ligand, having low steric requirements, allows greater stability of the *cis* isomer relative to that of the *trans* form. The higher stability of the *cis* isomer can be attributed to strong Mn–C π-bonding. In this isomer the CO's compete for the metal $d\pi$-orbitals with the relatively poorly π-bonding ligands, L. The *trans* isomer¹ is then of lower stability, since the *trans*-CO's must share the same $d\pi$-orbitals, resulting in weaker Mn–C bonds. In complexes bearing bulky ligands, the *cis* isomer is also probably favored by higher Mn–C bond energies, but the over-all equilibrium lies far toward the *trans* isomer as a result of entropy effects. The higher entropy of the *trans* form could result from an increase in freedom of motion of the ligands in the less hindered *trans* positions and/or from greater solvation of the more polar *cis* isomer.

It was likewise found in the *cis*–*trans* isomerization of $Mo(CO)_4[P(C_2H_5)_3]_2$, that at 45° the *cis* form isomerizes to an equilibrium mixture consisting of 80% *trans*.[9] In this system the *trans* structure is also thermodynamically more stable. In the same study, both *cis*- and *trans*-$Mo(CO)_4[P(C_6H_5)_3]_2$ were prepared. The *cis* isomer probably exists because, compared to Mn, the larger Mo atom reduces crowding of the $P(C_6H_5)_3$ groups.

A related study of the *cis* $\rightleftarrows$ *trans* equilibrium of $Pt[P(C_2H_5)_3]_2Cl_2$ gives $\Delta H = 2.5$ kcal./mole and $\Delta S = 13.3$ e.u.[10] Here too the bond energies of the *cis* isomer are estimated to be higher than those of the *trans*. That the equilibrium lies far toward *trans*-$Pt[P(C_2H_5)_3]_2Cl_2$ is a result of the large positive entropy of isomerization which is attributed to greater solvation of the more polar *cis* isomer. In this case, steric interactions were considered to be negligible because of the large platinum(II).

Kinetics and Mechanism of Isomerization.—The *cis* to *trans* isomerization of $Mn(CO)_3[P(OC_6H_5)_3]_2Br$ as shown by eq. 1 was studied kinetically and found to proceed at conveniently measurable rates at 40–70°

(9) R. Poilblanc and M. Bigorgne, *Bull. soc. chim.*, 1301 (1962).

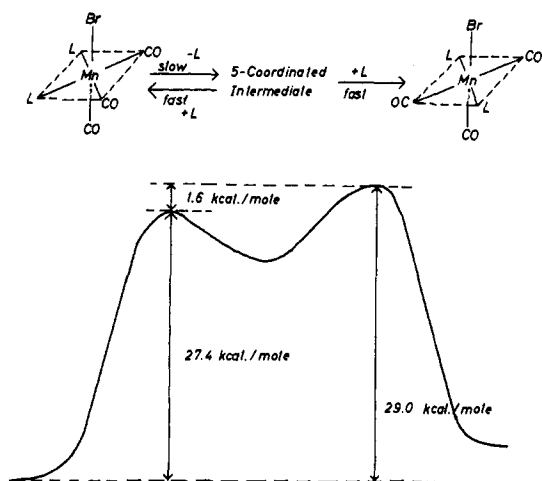(10) J. Chatt and R. G. Wilkins, *J. Chem. Soc.*, 4300 (1952).

Fig. 3.—Mechanism of isomerization of cis-Mn(CO)$_3$L$_2$Br where L = P(OC$_6$H$_5$)$_3$.

in a variety of organic solvents. In the solid state at 55°, the reaction was immeasurably slow.

Data in Table III show that the reaction is first order in complex, for there is only a very small change in the rate constant accompanying an almost tenfold change in concentration. Added P(OC$_6$H$_5$)$_3$ depresses the rate significantly, but this will be interpreted later as a slight modification of the primary mechanism.

The compound cis-Mn(CO)$_3$[P(OC$_6$H$_5$)$_3$]$_2$Br in TCE at 60° isomerizes with a rate constant of 1.71×10^{-4} sec.$^{-1}$ (Table III). However, when isomerization occurs in the presence of P(C$_6$H$_5$)$_3$, a much faster reaction (2.06×10^{-3} sec.$^{-1}$, without evolution of CO) occurs. The rate of this reaction is independent of the P(C$_6$H$_5$)$_3$ concentration (Table IV). The reaction results in the formation of an unknown product which could not be isolated by solvent precipitation and which decomposed during an attempted separation on a silica gel chromatography column. The infrared spectrum of this compound is different from that of either cis- or $trans$-Mn(CO)$_3$L$_2$Br and has absorption bands at 2092(m), 2008(s) and 1972(s) cm.$^{-1}$. This same product was obtained from the reaction of $trans$-Mn(CO)$_3$[P(OC$_6$H$_5$)$_3$]$_2$Br with P(C$_6$H$_5$)$_3$, but at a much slower rate (3.4×10^{-4} sec.$^{-1}$).

If cis-Mn(CO)$_3$[P(OC$_6$H$_5$)$_3$]$_2$Br is allowed to react with P(OC$_4$H$_9$)$_3$, a stepwise replacement of the P(OC$_6$H$_5$)$_3$ groups occurs as shown by the broadening of the infrared absorption bands during the formation of the mixed complex, cis-Mn(CO)$_3$[P(OC$_6$H$_5$)$_3$][P(OC$_4$H$_9$)$_3$]Br, followed by narrowing again with the final formation of cis-Mn(CO)$_3$[P(OC$_4$H$_9$)$_3$]$_2$Br. This isomer then isomerizes more slowly to $trans$-Mn(CO)$_3$[P(OC$_4$H$_9$)$_3$]$_2$Br with the expected rate, 3.4×10^{-5} sec.$^{-1}$. The rate constant for replacement of P(OC$_6$H$_5$)$_3$ is approximately 2×10^{-3} sec.$^{-1}$, as estimated from the rate of band broadening and narrowing. It thus appears that the same rate-determining step is involved in the reactions of cis-Mn(CO)$_3$[P(OC$_6$H$_5$)$_3$]$_2$Br with either P(C$_6$H$_5$)$_3$ or P(OC$_4$H$_9$)$_3$ (Table IV). Since both reactions are independent of the nature and concentration of the entering ligand, the rate of dissociation of P(OC$_6$H$_5$)$_3$ from the complex is presumably the slow step common to both reactions. However, the overall rate of isomerization of cis-Mn(CO)$_3$[P(OC$_6$H$_5$)$_3$]$_2$Br depends not only upon the rate of P(OC$_6$H$_5$)$_3$ dissociation but also upon the rates of forming the cis and $trans$ isomers from the resulting five-coördinated intermediate (Fig. 3). Thus, according to the above rates, for every twelve dissociations of P(OC$_6$H$_5$)$_3$ only one P(OC$_6$H$_5$)$_3$ enters to form $trans$-Mn(CO)$_3$-

[P(OC$_6$H$_5$)$_3$]$_2$Br, whereas eleven return to re-form the cis isomer.

The activation parameters for the dissociation of P(OC$_6$H$_5$)$_3$ have been determined from the reaction of cis-Mn(CO)$_3$[P(OC$_6$H$_5$)$_3$]$_2$Br with P(C$_6$H$_5$)$_3$ at several temperatures (Table IV): $E_a = 27.4 \pm 1.4$ kcal./ mole (average deviation limits) and $\Delta S^{\ddagger} = 9.1$ e.u. (Fig. 3). The activation energy for the formation of the $trans$ isomer from the five-coördinated intermediate is approximately 1.6 kcal./mole higher than that for the formation of the cis isomer. Since π-bonding of the metal d$_{xz}$, d$_{yz}$ and d$_{xy}$ orbitals with CO will tend to keep the OC–Mn–CO angle at 90°, energy will be required to widen this angle during the formation of the $trans$ isomer. On the other hand, formation of the cis isomer takes advantage of the most stable π-bonding configuration.

Added P(OC$_6$H$_5$)$_3$ (Table III) depresses the rate of isomerization of cis-Mn(CO)$_3$[P(OC$_6$H$_5$)$_3$]$_2$Br by a factor of about two. Even small amounts of P(OC$_6$H$_5$)$_3$ decrease the rates almost to the minimum value, and reactions in which the ratio of P(OC$_6$H$_5$)$_3$ concentration to complex concentration is at least one have the same slow rates. The effect is small but suggests an association between cis-Mn(CO)$_3$[P(OC$_6$H$_5$)$_3$]$_2$Br and P(OC$_6$H$_5$)$_3$. The associated species then undergoes isomerization with a rate of about half that of the free complex.

The effect of solvent on the rate of isomerization of cis-Mn(CO)$_3$[P(OC$_6$H$_5$)$_3$]$_2$Br is also very small (Table III), and this too supports the non-ionic mechanism postulated above. However, in the absence of solvent, no measurable isomerization occurs at these temperatures, so the solvent must mediate the transfer of P(OC$_6$H$_5$)$_3$, but is not involved in the activated complexes to a significant extent.

The rates of isomerization of cis-Mn(CO)$_3$L$_2$Br complexes, where L = P(C$_6$H$_5$)Cl$_2$, P(C$_4$H$_9$)$_3$, P(OC$_6$H$_5$)$_3$ and P(OC$_4$H$_9$)$_3$, have been measured and their activation parameters determined (Tables III and V).

TABLE V
ACTIVATION PARAMETERS FOR THE ISOMERIZATION OF
cis-Mn(CO)$_3$L$_2$Br IN TCE

L	E_a, kcal./mole^a	$\Delta S^{\ddagger}$ e.u.
P(C$_6$H$_5$)Cl$_2$	26.4 ± 2.3^b	3.0
P(C$_4$H$_9$)$_3$	$27.7 \pm 0.5^{b,c}$	3.8
P(OC$_6$H$_5$)$_3$	29.0 ± 1.1^d	9.1
P(OC$_6$H$_5$)$_3$	30.2 ± 0.7^b	12.1
P(OC$_4$H$_9$)$_3$	31.8 ± 0.3^b	14.3

^{a} Limits are average deviations. ^{b} Determined from limiting rates in the presence of excess L. ^{c} Measured in P(C$_4$H$_9$)$_3$ solvent. ^{d} In absence of added P(OC$_6$H$_5$)$_3$.

The activation energies increase with changing L in the order: P(C$_6$H$_5$)Cl$_2$ < P(OC$_6$H$_5$)$_3$ < P(OC$_4$H$_9$)$_3$. The P(C$_4$H$_9$)$_3$ compound has not been included in this series since it decomposes in TCE but isomerizes in P(C$_4$H$_9$)$_3$ solvent. The above trend seems to indicate that the best π-bonding ligands[11] isomerize most readily to the $trans$ structure. This is reasonable since the better π-bonding ligands tend to stabilize to a greater extent an activated complex in which the entering ligand approaches from the direction $trans$ to the phosphine remaining in the five-coördinated intermediate. However, these activation energies are a composite of the activation energy for the dissociation of L from the cis complex and the difference in activation energies between the reactions of the five-coördinated intermediate with L to form the cis or $trans$ isomer. As seen from the discussion for cis-Mn(CO)$_3$-[P(OC$_6$H$_5$)$_3$]$_2$Br, the activation energy of the dissocia-

(11) M. Bigorgne, Bull. soc. chim., 1986 (1960).

tion is the larger term, but whether it determines the above trend is not known. An attempt to measure the activation energy for the dissociation of $P(OC_4H_9)_3$ from cis-$Mn(CO)_3[P(OC_4H_9)_3]_2Br$ was made using the method employed for the $P(OC_6H_5)_3$ complex. Thus $P(C_6H_5)_3$ was added to a solution of cis-$Mn(CO)_3$-$[P(OC_4H_9)_3]_2Br$, but in this case no reaction occurred, and the isomerization proceeded as usual.

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The Mercury(³P₁)-Sensitized Photolysis of Some Liquid Alkanes at 25°[1]

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The liquid phase mercury-photosensitized decompositions of n-hexane, n-pentane, isopentane, 3-methylpentane, 2,2-dimethylbutane, and 2,3-dimethylbutane have been investigated. The mechanism of this liquid phase photolysis is similar to that of the low temperature vapor phase investigations. The photolysis products are hydrogen, parent olefin, and parent dimer with no carbon–carbon cracking products. One primary process associated with the quenching of Hg(³P₁) atoms is the formation of a mercury complex. This complex and product olefins alter the "effective" mercury concentration while trace impurities completely remove a large fraction of it. Quantum yields for hydrogen production are all nearly one, indicating complete quenching of excited mercury atoms. Olefin products have a quantum yield of about 0.4 for hydrocarbons containing only secondary and primary H-atoms. The presence of tertiary H-atoms increases the olefin yield considerably. This increase is reflected in the k_{disp}/k_{comb} which is less than 1 for secondary and primary radicals and greater than 2.5 for tertiary radicals. The precursors for dimer products are tertiary, secondary, and primary radicals. Tertiary–tertiary dimers are most important, but primary radical combinations become significant as the ratio of primary H atoms to secondary and tertiary H-atoms increases.

I. Introduction

Information regarding the reactions of large alkyl radicals in the liquid phase is meager. Production of these radicals by radiolysis and by chemical means usually is accompanied by the simultaneous production of a variety of products which obscure the radical reactions. A study of the liquid phase mercury-photosensitization of n-decane[2] indicated that the sole precursors of the final products were parent alkyl radicals and H-atoms. This technique thus should be suited for unambiguous study of alkyl radicals in the liquid phase.

In order for mercury-photosensitization to be a practical tool for the study of liquid phase decompositions, it is necessary that mercury be sufficiently soluble in the solvent to absorb significant quantities of incident light during a reasonable period of irradiation. Some solutions of mercury in hydrocarbons have been shown[2,3] to extinguish much of the 2537-Å. mercury resonance radiation. Solubilities of mercury in various hydrocarbons[4] all lie in the micromolar concentration range and vary only slightly from one hydrocarbon solvent to another. Absorption spectra of mercury in the hydrocarbons used for this investigation were found to be similar to one another and to exhibit the pressure broadenings and Stark effect splittings observed previously.[2,3] These hydrocarbon–mercury solutions all absorb approximately 4% of the incident 2537-Å. radiation for each centimeter of path length.

Phibbs and Darwent[2] did not observe any C–C "atomic" cracking products or olefin products in the liquid phase mercury-photosensitized decomposition of n-decane, while similar vapor phase decompositions show that both types of products are important. The absence of liquid phase C–C "atomic" cracking products is in agreement with the low temperature vapor phase investigations of Taylor and Bates[5] and Back,[6] and

may be explained in terms of solvent stabilization effects, but the absence of olefin products in the n-decane system is surprising.

This investigation was initiated in an effort to evaluate the applicability of mercury-photosensitized decompositions to the liquid phase and to clarify the reaction mechanism by careful product analysis on a number of saturated hydrocarbon systems. Because additional information concerning the photosensitization process is needed, a third important facet of this investigation was an attempt to elucidate this mechanism.

II. Experimental

The light source used in these experiments was an Sc2537 low pressure mercury vapor lamp manufactured by the Hanovia Manufacturing Co. It is constructed of a Vycor envelope shaped into a four-coil spiral, a geometry identical with those lamps described in an earlier research from this Laboratory.[7] Its output is 95% at 2537 Å. with small intensities at longer wave lengths.

Three reaction vessels were employed. All rate studies were carried out in a vessel consisting of a Vycor tube closed at one end and surrounded by a Vycor water jacket. The inner tube was connected to a Pyrex–Vycor graded seal to facilitate manipulation. A small side arm was attached to the vessel above the graded seal so mercury might be isolated from the system during filling and photolysis. The reaction volume of this vessel was 6.7 cc. Experiments requiring optical density measurements were performed in a vessel having similar construction, but with a reaction volume of 60 cc. and a 100-mm. quartz absorption cell fused to the vessel below the graded seal. A few experiments which involved high conversions were made in a 200-cc. Vycor vessel without a water jacket. This cell was attached to a 300-cc. ballast vessel to prevent the build-up of product pressure. Lamp intensity was measured by the uranyl oxalate actinometer using the modification of Pitts, et al.[8] A number of measurements at several optical densities indicated a linear variation of absorbed intensity with optical density in the cylindrical vessels at the low optical densities possible in these experiments. Maximum output of the lamp was reached in 2 min., and corrections for this build-up time were negligible compared to photolysis times. For quantum yield determinations, it was necessary to take a time average of the absorbed intensity by measurement of the variation in optical density of the mercury–hydrocarbon system.

(1) Based upon thesis research submitted by Robert R. Kuntz in partial fulfillment of the requirements for the degree of Doctor of Philosophy, Carnegie Institute of Technology.

(2) M. K. Phibbs and B. deB. Darwent, J. Chem. Phys., 18, 679 (1950).

(3) H. Reichardt and K. F. Bonhoeffer, Z. Physik, 67, 780 (1931).

(4) H. C. Moser and A. Voigt, U. S. Atomic Energy Comm. I.S.C.-892 (1957).

(5) H. S. Taylor and J. R. Bates, Proc. Natl. Acad. Sci., 12, 714 (1926).

(6) R. A. Back, Trans. Faraday Soc., 54, 512 (1958).

(7) D. B. Peterson and G. J. Mains, J. Am. Chem. Soc., 81, 3510 (1959).

(8) J. N. Pitts, Jr., J. D. Margerum, R. P. Taylor and W. Brum, ibid., 77, 5499 (1955).