

shows a slight increase compared to $(C_5H_5)Fe(CO)_2Br$. By analogy with the series $[(C_5H_5)Fe(CO)X]_2DPPA$ and $(C_5H_5)Fe(CO)_2X$ we would have expected $[(C_5H_5)Fe(CO)SnCl_3]_2DPPA$ to have a higher isomer shift than the corresponding compound $(C_5H_5)Fe(CO)_2SnCl_3$. In these complexes, however, isomer shifts and quadrupole coupling constants will be dependent on the detailed stereochemistry at both tin and phosphorus atoms. Thus interaction of $SnCl_3^-$ and $(C_6H_5)_2P$ might be expected to decrease the Cl-Sn-Cl and C-P-C angles resulting in increased "s" contributions to the Sn-Fe and P-Fe bonds and a consequent smaller isomer shift. Since the X-ray study⁶ of $[(C_5H_5)_2Fe_2(CO)_3]_2DPPA$ shows considerable steric interaction between the π - C_5H_5 and $(C_6H_5)_2P$ groups, a similar distortion is likely in the tin compound. Moreover the molecular structure of $[(C_5H_5)Fe(CO)_2]_2SnCl_2$ indicates a marked deviation from tetrahedral geometry at the tin atom with a Cl-Sn-Cl angle of $94^\circ 10'$.²² This distortion at the tin atom is reflected in the large quadrupole splitting in the ^{119}Sn Mössbauer spectrum (Table II). Although a direct comparison of parameters for $[(C_5H_5)Fe(CO)_2]_2SnCl_2$ and $[(C_5H_5)Fe(CO)SnCl_3]_2DPPA$ is inadvisable in view of the different symmetry at the tin atom in each case, the data in Table II clearly suggest a larger distortion at the tin atom in $[(C_5H_5)Fe(CO)SnCl_3]_2DPPA$ than in $(C_5H_5)Fe(CO)_2SnCl_3$. Complete X-ray data for this series would be interesting.

Mössbauer parameters for $(C_5H_5)FeBr[P(OCH_3)_3]_2$ illustrate the effect of replacing the two carbonyl groups

(22) J. E. O'Connor and E. R. Corey, *Inorg. Chem.*, **6**, 968 (1967).

of $(C_5H_5)Fe(CO)_2Br$ with $P(OCH_3)_3$. The increase in isomer shift reflects the lower π -bonding ability of the $P(OCH_3)_3$ group compared to CO. A more distorted iron environment and higher quadrupole splitting are also noticeable for the phosphite complex.

The Mössbauer spectrum of $[\{(C_5H_5)Fe(CO)_2\}_2DPPA](FeBr_4)_2$ gives excellent confirmation of the ionic formulation. The spectrum reveals two kinds of iron atom, one with a lower isomer shift and highly distorted environment, the other with a higher shift and symmetric environment. The more symmetric iron atom has the same isomer shift as $FeBr_4^-$.²³ Replacement of $FeBr_4^-$ by $FeCl_4^-$ gave a further single resonance, isomer shift 0.50 mm/sec characteristic of the $FeCl_4^-$ ion (lit.²⁴ value 0.55 mm/sec). Replacement of the anions in $[\{(C_5H_5)Fe(CO)_2\}_2DPPA](FeX_4)_2$ by PF_6^- removed the single unsplit resonances from the spectra. For the iodide $[\{(C_5H_5)Fe(CO)_2\}_2(DPPA)](I_3)_2$ no absorption due to tetrahedral iron(III) was observed. It can be seen that the asymmetric iron site in the $FeCl_4^-$, $FeBr_4^-$, I_3^- , and PF_6^- derivatives remains unaffected by anion changes and the parameters for the cation $[(C_5H_5)Fe(CO)_2]_2DPPA^{2+}$ are very similar to those of the analogous unsubstituted carbonyl derivative $(C_5H_5)Fe(CO)_3^+$.

Acknowledgment.—We acknowledge the support of the National Research Council of Canada.

(23) C. A. Clausen, III, and M. L. Good, "Mössbauer Effect Methodology," Vol. 4, I. J. Gruverman, Ed., Plenum Press, New York, N. Y., 1968, p 197.

(24) G. M. Bancroft, A. G. Maddock, W. K. Ong, and R. H. Prince, *J. Chem. Soc., A*, 723 (1966).

Notes

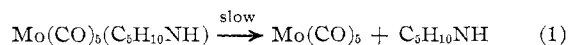
CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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Kinetics and Mechanism of the Thermal Decomposition Reactions of the *trans*-Bis(triphenylphosphine)manganese Tricarbonyl Halides¹

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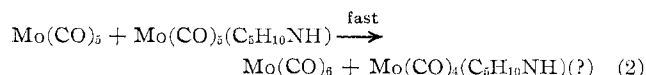
Recently, Darensbourg and Brown reported³ kinetic data for the thermal decomposition of $Mo(CO)_5(C_6H_{10}NH)$ to form $Mo(CO)_6$ and proposed that the decomposition proceeded by the two-step mechanism shown in the equations



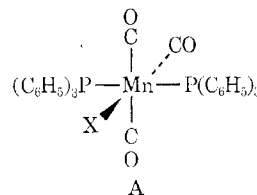
(1) This research was supported by a grant from the National Research Council of Canada.

(2) Holder of a National Research Council of Canada postgraduate scholarship, 1967–present.

(3) D. J. Darensbourg and T. L. Brown, *Inorg. Chem.*, **7**, 1679 (1968).



The net result of the decomposition was the replacement of piperidine by CO. We have been investigating the thermal decomposition reactions of some other metal carbonyl complexes in which a coordinated ligand is substituted by CO. In this note, we present kinetic data for the thermal decomposition reactions of the *trans*- $Mn(CO)_3[P(C_6H_5)_3]_2X$ ($X = Cl, Br, I$) derivatives (A) in *s*-tetrachloroethane at 40.0–



60.0° to give *cis*- $Mn(CO)_4[P(C_6H_5)_3]_2X$ and suggest a possible mechanism for the reactions.

Experimental Section

The *trans*- $Mn(CO)_3[P(C_6H_5)_3]_2X$ complexes were prepared by maintaining a chloroform solution of the appropriate Mn-

(CO)₅X complex and a five-tenfold excess of P(C₆H₅)₃ at 60–80° until the ir spectrum of the reaction mixture in the C–O stretching region corresponded principally to that of the desired product. (A small amount of *cis*-Mn(CO)₄[P(C₆H₅)₃]X was almost always present at this time.) The products were retrieved from solution by following the method outlined in the literature for similar complexes⁴ and recrystallized until analytically pure.

The *s*-tetrachloroethane was purified as described in the literature.⁵

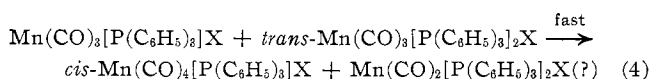
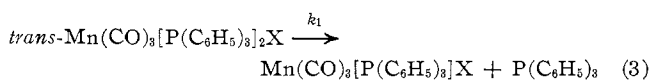
Kinetic data were obtained by monitoring the rate of decrease of the lowest energy C–O stretching absorption of each substrate (~1914 cm⁻¹) using a Perkin-Elmer Model 337 grating infrared spectrophotometer. Solutions of the substrates were prepared in aluminum foil wrapped⁶ Schlenk tubes fitted with neoprene serum caps and thermostated in a constant-temperature bath. Samples were withdrawn with a syringe at appropriate intervals and their spectra were scanned in the C–O stretching region. The rate of decomposition of *trans*-Mn(CO)₃[P(C₆H₅)₃]₂Br at 50.0° was also measured by following the rate of decreasing absorbance of the band at 449 mμ in the visible spectrum. The rates obtained by the two different methods were virtually identical. The visible spectra were recorded on a Coleman-Hitachi Model 124 uv-visible spectrophotometer coupled to an external recorder.

Linear first-order plots of ln(A – A_∞), where A is the absorbance at time t and A_∞ is the absorbance at infinite time, vs. t were obtained. The reactions went to completion and the plots were linear to 75–85% completion, except for *trans*-Mn(CO)₃[P(C₆H₅)₃]₂I for which significant deviations began to appear after 50% completion. In the latter case the reaction product, *cis*-Mn(CO)₄[P(C₆H₅)₃]I, was decomposing further to form Mn(CO)₅I⁷ presumably with regeneration of the starting material, *trans*-Mn(CO)₃[P(C₆H₅)₃]₂I.

The rate constants were calculated using a least-squares computer program and are considered to be accurate to about ±10%.

Results and Discussion

The observed rate constants (*k*_{obsd}) given in Table I indicate a first-order dependence on substrate concentration. The associated activation entropies (Table I, footnotes a, b, and f) are in the range expected for an SN1 dissociative mechanism.⁸ These experimental results are in accord with the mechanism shown in eq 3 and 4 involving the rupture of an Mn–P bond as the slow rate-determining step



Provided that the decomposition reactions go to completion, the observed rate constant will be given by *k*_{obsd} = 2*k*₁. This mechanism is similar to that proposed by Darensbourg and Brown⁹ for the decomposition of Mo(CO)₅(C₅H₁₀NH) (eq 1 and 2).

None of the C–O bands observed in any of the ir spectra of the reaction mixtures taken during the kinetic runs was attributable to dicarbonyl species of the type Mn(CO)₂[P(C₆H₅)₃]₃X. It appears that

TABLE I
FIRST-ORDER RATE CONSTANTS FOR THE DECOMPOSITION REACTIONS OF *trans*-Mn(CO)₃[P(C₆H₅)₃]₂X IN *s*-TETRACHLOROETHANE

X	10 ³ × concn, M	Temp, °C	10 ³ <i>k</i> _{obsd} , sec ⁻¹
Cl ^a	3.79	40.0	0.89
	3.86	50.0	3.3
	6.95		2.7
Br ^b	2.82	60.0	9.6
	4.01	40.0	0.60
	1.34	50.0	2.9 ^c
	1.50		2.8
	2.35		2.8
	2.36		2.8
	2.36		2.7 ^d
	2.44		1.3 ^e
	3.01		2.6
	4.72		2.0 ^d
	4.80		2.3
I ^f	6.10		2.1
	6.59		2.2
	3.53	60.0	10
	3.54	40.0	0.65
	3.76	50.0	2.3
	5.20		2.0
	3.26	60.0	9.5

^a Δ*H*[‡] = 25 ± 2 kcal mol⁻¹ and Δ*S*[‡] = -2 ± 4 eu. ^b Δ*H*[‡] = 29 ± 2 kcal mol⁻¹ and Δ*S*[‡] = 12 ± 4 eu. ^c From following changes in the visible spectrum. ^d In the presence of CO. ^e In the presence of 0.0103 M P(C₆H₅)₃. ^f Δ*H*[‡] = 28 ± 2 kcal mol⁻¹ and Δ*S*[‡] = 7 ± 4 eu.

either these dicarbonyl species or the intermediates, Mn(CO)₂[P(C₆H₅)₃]₂X, rapidly decomposed under the experimental conditions employed. In agreement with the proposed mechanism, the yield (calculated from a Beer's law plot) of *cis*-Mn(CO)₄[P(C₆H₅)₃]Br always represented 40–50% of the concentration of the starting material, *trans*-Mn(CO)₃[P(C₆H₅)₃]₂Br. Furthermore, as expected, the rate of decomposition was retarded by the presence of excess P(C₆H₅)₃ (Table I, footnote e). When the decomposition of *trans*-Mn(CO)₃[P(C₆H₅)₃]₂Br was carried out under an atmosphere of CO, the yield of *cis*-Mn(CO)₄[P(C₆H₅)₃]Br increased from the usual 40–50% to about 85% without any apparent effect on the decomposition rate. The increased yield of *cis*-Mn(CO)₄[P(C₆H₅)₃]Br presumably arises because CO successfully competes with a molecule of starting material for the intermediate Mn(CO)₃[P(C₆H₅)₃]Br, and so reaction 4 is no longer the only way in which *cis*-Mn(CO)₄[P(C₆H₅)₃]Br can be formed.

Furthermore, if reaction 4 is diminished in the presence of CO, the rate of decomposition of *trans*-Mn(CO)₃[P(C₆H₅)₃]₂Br should be slower than usual. That this was not observed is presumably because the decrease in decomposition rate was fairly small and fell within the limits of experimental error of the method used for rate determination.

A referee suggested an alternative mechanism for the decomposition reactions that would be consistent with the observations discussed so far. This mechanism is shown in eq 5–7 and involves two concomitant rate-determining steps: the rupture of an Mn–P bond and of an Mn–C bond. The observed rate constant

(4) R. J. Angelici, F. Basolo, and A. J. Poe, *J. Am. Chem. Soc.*, **85**, 2215 (1963).

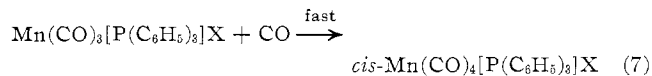
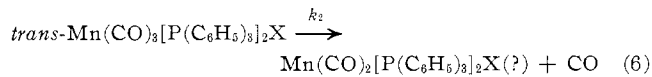
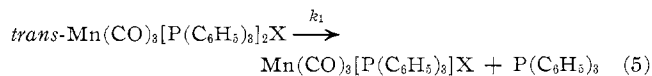
(5) A. I. Vogel, "A Textbook of Practical Organic Chemistry," Longmans, Green and Co., London, England, 1954.

(6) The decomposition was found to be slightly catalyzed by light and the reactions were therefore carried out in the dark.

(7) H. K. Spendjian and I. S. Butler, unpublished results.

(8) R. J. Angelici, *Organometal. Chem. Rev.*, **3**, 173 (1968).

for this mechanism (assuming that the reactions go to completion) will be given by $k_{\text{obsd}} = k_1 + k_2$. How-



ever, when the decomposition of *trans*-Mn(CO)₃[P(C₆H₅)₃]₂Br was studied in the presence of C¹⁸O, the substrate ir band at 1951 cm⁻¹ was observed to disappear qualitatively at a much faster rate than normal and a band due to a C¹⁸O-substituted species rapidly appeared at approximately 1930 cm⁻¹. These observations suggest that the rate of CO substitution is significantly faster than the rate of decomposition and therefore we favor our proposed mechanism over that indicated by the referee.

In sharp contrast to the rates of the CO substitution reactions of Mn(CO)₃X^{9,10} and *cis*-Mn(CO)₄LX¹¹ [L = P(C₆H₅)₃, Sb(C₆H₅)₃, etc.] which decrease dramatically with changes in X in the order Cl > Br > I, the rates of the decomposition reactions of *trans*-Mn(CO)₃[P(C₆H₅)₃]₂X were little affected by changes in X. The decrease in the CO substitution rates with the increasing atomic weight of X has been explained in terms of the electronegativities of the X atoms—the lower the electronegativity of the X atom, the greater the electron density on the manganese atom available for back-bonding to the carbonyl groups, and consequently the stronger the Mn–C bonds. If the Mn–P bond strengths in the *trans*-Mn(CO)₃[P(C₆H₅)₃]₂X compounds are significantly dependent on π bonding, it would be reasonable to expect the observed decomposition rates to show some dependence on X. However, as this was not found to be the case, it appears that the Mn–P bond strengths in the tricarbonyl halides stem mainly from σ- rather than π-bonding effects. Other workers have reached the same conclusion concerning the Mo–P,¹² W–P,^{13,14} and Ni–P¹⁵ bond strengths in molybdenum, tungsten, and nickel carbonyl complexes.

The thermal decomposition of *trans*-Mn(CO)₃[P(OC₆H₅)₃]₂Br was also studied. However, contrary to what would be predicted from the lower basicity and resultant poorer σ-bonding ability of P(OC₆H₅)₃ by comparison with P(C₆H₅)₃,¹³ the reaction proceeded extremely slowly ($t_{1/2} \gg 24$ hr). P(OC₆H₅)₃ has also been found to be anomalous in its behavior in the substitution reactions of *trans*-Mo(CO)₄L₂ [L = P(OC₆H₅)₃ and P(C₆H₅)₃].¹²

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

(10) R. J. Angelici and F. Basolo, *ibid.*, **84**, 2495 (1962).

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

(12) F. Zingales, F. Canziani, and F. Basolo, *J. Organometal. Chem. (Amsterdam)*, **7**, 461 (1967).

(13) R. J. Angelici and C. M. Ingemanson, *Inorg. Chem.*, **8**, 83 (1969).

(14) R. J. Angelici and M. D. Malone, *ibid.*, **6**, 1731 (1967).

(15) L. S. Meriwether and M. L. Fiene, *J. Am. Chem. Soc.*, **81**, 4200 (1959).

In an effort to extend the study, the synthesis of *trans*-Mn(CO)₃[Sb(C₆H₅)₃]₂Br was attempted. However, only the *cis* complex could be isolated, contrary to what had been previously predicted.⁴ Dobson and Houk have recently found¹⁶ that substituted molybdenum carbonyls tend to form *cis* complexes with Sb(C₆H₅)₃ and *trans* complexes with P(C₆H₅)₃ and As(C₆H₅)₃ and attributed the difference to the larger size of the Sb atom. Heating a solution of *cis*-Mn(CO)₃[Sb(C₆H₅)₃]₂Br did afford *cis*-Mn(CO)₄[Sb(C₆H₅)₃]Br but the decomposition appears to be much more complex than the decomposition of the *trans*-Mn(CO)₃[P(C₆H₅)₃]₂X compounds, as a simple rate plot was not obtained.

(16) R. Dobson and L. W. Houk, *Inorg. Chim. Acta*, **1**, 287 (1967).

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Mössbauer and Infrared Spectra of Tin(IV) Complexes of 2-Pyridinethiol 1-Oxide

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The anion of 2-pyridinethiol 1-oxide is an excellent complexing agent for a variety of metal ions. O→M dative bond formation in these complexes is indicated by a decrease in frequency of the absorption attributed to the N–O stretching vibration in the 1200-cm⁻¹ region and by absorptions associated with the oxygen-metal stretching vibrations. Mössbauer spectra of tin(IV) complexes containing this ligand give an indication of their configuration and electron distribution.

Experimental Section

Preparation of Compounds.—Tin(IV) fluoride, bromide, and iodide and di-*n*-butyltin dichloride and diphenyltin dichloride were obtained from Alfa Inorganics, Inc. Anhydrous tin(IV) chloride was a J. T. Baker Co. product. The sodium salt of 2-pyridinethiol 1-oxide was obtained from Matheson Coleman and Bell.

Bis(2-pyridinethiolato 1-oxide)di-*n*-butyltin(IV) was prepared by mixing absolute ethanol solutions of the sodium salts of 2-pyridinethiol 1-oxide and di-*n*-butyltin dichloride in a 2:1 ratio. The product was crystallized from benzene and melted at 94–96°. The corresponding diphenyl compound was prepared from methanol solutions; the product melted above 210°. Isothiocyanato(2-pyridinethiolato 1-oxide)diphenyltin(IV) was prepared by refluxing a chloroform solution, 50 ml, containing 2 mmol each of diphenyltin diisothiocyanate² and 2-pyridinethiol 1-oxide. The solution was filtered and the filtrate was added with stirring to 200 ml of hexane. The white precipitate that formed was dried under vacuum at 56°. The dihalobis(2-pyridinethiolato 1-oxide)tin(IV) complexes were prepared by mixing methanol solutions of the tin(IV) halide and the sodium salt of 2-pyridinethiol 1-oxide, 0.025 and 0.05 *M*, respectively.

(1) The Radiation Laboratory is operated by the University of Notre Dame under contract with the Atomic Energy Commission. This is AEC Document No. COO-38-692.

(2) M. A. Mullins and C. Curran, *Inorg. Chem.*, **7**, 2584 (1968).