ride in the presence of the electrophilic catalyst, aluminum chloride, is the exchanging moiety. The lack of detectable exchange between pentaborane-9 and silane-d_4 at room temperature indicates a higher activation energy for hydrogen transfer than required for the pentaborane-9–deuterium chloride–aluminum chloride system.

Acknowledgment.—Appreciation is expressed for the partial support of this work by the Office of Naval Research under Contract Nonr-908(14), Task NR 052-410.

CONTRIBUTION FROM NOYES CHEMICAL LABORATORY,
UNIVERSITY OF ILLINOIS, URBANA, ILLINOIS 61801

Kinetics of the Thermal Decomposition and Substitution Reactions of Molybdenum Pentacarbonyl Amine Compounds[1]

BY D. J. DARENSBOURG[2] AND THEODORE L. BROWN

Received March 26, 1968

Kinetic studies of the substitution reactions of $Mo(CO)_6$ with phosphines and amines indicate that these substitutions proceed by an SN1 mechanism at low ligand concentrations (less than 0.025 *M*).[3] However at concentrations greater than 0.050 *M* both first- and second-order kinetics are observed.[4] The rate of the reactions obeys the following rate law, where k_1 and k_2 are described in eq 1 and 2.

$$\text{rate} = [k_1 + k_2(\text{L})][\text{Mo(CO)}_6]$$

$$\text{Mo(CO)}_6 \xrightarrow{k_1} \text{Mo(CO)}_5 + \text{CO} \xrightarrow[\text{L}]{\text{rapid}} \text{Mo(CO)}_5\text{L} \qquad (1)$$

$$\text{Mo(CO)}_6 + \text{L} \xrightarrow{k_2} \text{Mo(CO)}_5\text{L} + \text{CO} \qquad (2)$$

We have found that $Mo(CO)_5C_5H_{10}NH$ and $Mo(CO)_5C_5H_5N$ decompose in solution to give $Mo(CO)_6$ at room temperature. The kinetics for the decomposition of $Mo(CO)_5C_5H_{10}NH$ alone and in the presence of phosphorus ligands have been studied.

Experimental Section

The decomposition reactions were qualitatively followed by observing the disappearance of bands in the CO stretching region of the infrared spectra. Simultaneously the appearance of bands due to $Mo(CO)_6$ or phosphorus-substituted $Mo(CO)_6$ was observed. These measurements were taken at the temperature of the cell compartment of the Beckman IR-7 instrument, which varied from 43 to 46°. The infrared spectra were employed only for product identification and concentration.

Quantitative rate data for both decomposition and substitution were obtained on a Cary Model 15 by observing the disappearance of the characteristic band at 397.5 mμ in the visible spectrum of $C_5H_{10}NHMo(CO)_5$. Constant temperature was maintained by means of a close-fitting brass block mounted in the cell compartment. The temperature of the block was maintained by a flow of thermostated water through internal holes and was measured by means of an NBS Certified thermometer.

The complexes were prepared as previously described.[5] Solvents were spectral grade hexane or carbon disulfide, used without further treatment.

Linear first-order plots of ln $(A - A_\infty)$, where A is the absorbance at time t and A_∞ is the absorbance at infinite time, *vs.* t were obtained. These plots were linear for at least 75% reaction completion. All data were subjected to a least-squares treatment.

Results and Discussion

The quantities of $Mo(CO)_6$ present upon completion of three kinetic runs involving $Mo(CO)_5C_5H_{10}NH$ in carbon disulfide, at concentrations of 2.056, 3.029, and 3.627×10^{-4} *M*, represented 48.6, 49.5, and 50.8%, respectively, of the starting material. Rate constants for the decomposition reaction in both hexane and carbon disulfide solvents at various temperatures are listed in Table I.

TABLE I
FIRST-ORDER RATE CONSTANTS FOR THE DISSOCIATION OF $Mo(CO)_5C_5H_{10}NH$

In hexane		In carbon disulfide	
Temp, °C	10^5k_1, sec^{-1}	Temp, °C	10^5k_1, sec^{-1}
33.5	1.49	33.5	7.27
39.6	3.17	39.9	15.40
40.0	3.15	49.7	39.60
43.4	4.80		
49.8	10.48		

No quantitative rate data were obtained for the decomposition of $Mo(CO)_5C_5H_5N$ to $Mo(CO)_6$, but qualitatively the reaction was observed from the infrared studies to proceed at a slightly faster rate than for $Mo(CO)_5C_5H_{10}NH$.

We propose that the decomposition proceeds *via* a rate-determining dissociation, analogous to reaction 1 for the substitution reactions

$$\text{Mo(CO)}_5\text{C}_5\text{H}_{10}\text{NH} \xrightarrow{\text{slow}} \text{Mo(CO)}_5 + \text{C}_5\text{H}_{10}\text{NH} \qquad (3)$$

$$\text{Mo(CO)}_5\text{C}_5\text{H}_{10}\text{NH} + \text{Mo(CO)}_5 \xrightarrow{\text{rapid}} \text{Mo(CO)}_6 + \text{Mo(CO)}_4\text{C}_5\text{H}_{10}\text{NH (?)} \qquad (4)$$

No evidence for the presence of $Mo(CO)_4[C_5H_{10}NH]_2$ was obtained from the infrared spectra. Since the yield of $Mo(CO)_6$ upon completion of the decomposition reaction is 50%, it appears that the product of a CO abstraction, $Mo(CO)_4[C_5H_{10}NH]$, is not stable and rapidly decomposes to insoluble, metal-containing material. A precipitate is seen upon completion of the reaction, but no attempts were made at identification. Addition of excess piperidine stabilizes the $Mo(CO)_5C_5H_{10}NH$ species. For example, the presence of 0.08 *M* piperidine results in no measurable production of $Mo(CO)_6$ after several hours.

Addition to the reaction mixture of a second metal carbonyl compound, $Co(CO)_4SiCl_3$, stable with respect to thermal decomposition under the reaction conditions,

---

[1] This research was supported in part by a grant from the National Science Foundation.

[2] National Institutes of Health Predoctoral Fellow, 1967–1968.

[3] H. Werner, *J. Organometal. Chem.* (Amsterdam), **5**, 100 (1966).

[4] R. J. Angelici and J. R. Graham, *J. Am. Chem. Soc.*, **88**, 3658 (1966).

[5] D. J. Darensbourg and T. L. Brown, *Inorg. Chem.*, **7**, 959 (1968).

results in an enhancement in yield of $Mo(CO)_6$, but does not result in a change in decomposition rate.[6] A yield of 85% $Mo(CO)_6$ was obtained for a solution in which the concentration of $Co(CO)_4SiCl_3$ was about 0.005 *M*.

All of these experimental results are supportive of the proposed reaction pathway, as indicated in eq 3 and 4. It is of interest to compare the activation parameters for dissociation of amine with those for CO dissociation from $Mo(CO)_6$, Table II. The dissociation of amine is more facile in carbon disulfide as compared with hexane, probably because of solvent assistance in the dissociative process. A similar solvent effect is observed in substitution reactions of nickel carbonyl.[7]

Table II

Activation Parameters for the Dissociative Process

Compound	Solvent	ΔH_1^*, kcal/mol	ΔS_1^*, eu
$Mo(CO)_6$[a]	Decalin	31.7 ± 1.4	6.7 ± 3.7
$Mo(CO)_5C_5H_{10}NH$	Hexane	23.6 ± 1	5.4 ± 3
$Mo(CO)_5C_5H_{10}NH$	Carbon disulfide	19.9 ± 1	-10.3 ± 3

[a] J. R. Graham and R. J. Angelici, *Inorg. Chem.*, **6,** 2082 (1967).

We have also studied the effect of adding much stronger nucleophiles such as phosphines or phosphites on the reaction kinetics. The addition of these at concentrations <0.1 *M* resulted in the formation of $Mo(CO)_5L$ compounds in very good yield, where L = PF_3, $(n\text{-}C_4H_9)_3P$, $(CH_3O)_3P$, and $(C_6H_5O)_3P$. Results for $(n\text{-}C_4H_9)_3P$ and $(C_6H_5O)_3P$ additions are seen in Table III.

Table III

Results of Reactions of $(n\text{-}C_4H_9)_3P$ and $(C_6H_5O)_3P$ with $Mo(CO)_5C_5H_{10}NH$ in Hexane

Reactants		Yields
$Mo(CO)_5C_5H_{10}NH$	2.04×10^{-4} *M*	93% $(n\text{-}C_4H_9)_3PMo(CO)_5$
+		+
$(n\text{-}C_4H_9)_3P$	0.0865 *M*	3–7% *cis*-$[(n\text{-}C_4H_9)_3P]_2$-$Mo(CO)_4$[a]
		No $Mo(CO)_6$
$Mo(CO)_5C_5H_{10}NH$	2.16×10^{-4} *M*	85% $(C_6H_5O)_3PMo(CO)_5$
+		+
$(C_6H_5O)_3P$	0.0052 *M*	2–3% $Mo(CO)_6$

[a] Identified by its infrared spectrum in hexane. Bands were present at 1888.1, 1900.3, 1914.6, and 2014.6 cm^{-1}. These are of the correct relative intensities as compared with bands of other *cis*-$Mo(CO)_4L_2$ compounds and the frequencies are in agreement with those reported: F. Zingales, F. Canziani, and F. Basolo, *J. Organometal. Chem.* (Amsterdam), **7,** 461 (1967).

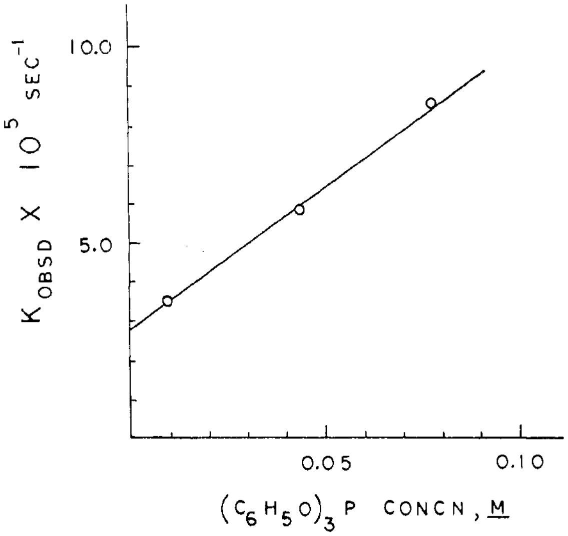

Figure 1.—Variation of k_{obsd} with ligand concentration for the reaction of $Mo(CO)_5C_5H_{10}NH$ with $(C_6H_5O)_3P$ in hexane at 40.0°.

$Mo(CO)_4(dipy)$ has been found to undergo substitution reactions under rather mild conditions with phosphites to yield *cis*-$Mo(CO)_3(L)(dipy)$ and *trans*-$Mo(CO)_4L_2$ compounds.[8] By contrast, spectral evidence for a mixed species of the type $Mo(CO)_4(L)$-$(C_5H_{10}NH)$ was not observed by us for the reactions of $Mo(CO)_5C_5H_{10}NH$ with the ligands (L) employed.

The rate of reaction of $Mo(CO)_5C_5H_{10}NH$ with a particular L was found to depend on the concentration of the nucleophile and increased in the order of increasing nucleophilicity: $(n\text{-}C_4H_9)_3P > (CH_3O)_3P > (C_6H_5O)_3P > PF_3$.

The dependence of the pseudo-first-order rate constant on the concentration of L in hexane is seen in Figure 1 where L = $(C_6H_5O)_3P$. k_2 for this substitution reaction is 6.02×10^{-4} M^{-1} sec^{-1} at 40.0°. This is substantially greater than that obtained for the comparable reaction between $(C_6H_5O)_3P$ and $Mo(CO)_6$, 1.48×10^{-4} M^{-1} sec^{-1} at 112.0°.[7] A value of $k_1 = 2.75 \times 10^{-5}$ sec^{-1} was obtained as intercept from the plot of k_{obsd} *vs.* [L], in good agreement with that for the dissociation of $Mo(CO)_5C_5H_{10}NH$ (Table I).

In summary, the present results demonstrate a similarity in the mechanisms of substitution for $Mo(CO)_5$-(amine) and $Mo(CO)_6$ compounds. The results provide a comparison of the energetics for dissociation of a strongly π-bonded ligand, CO, and a ligand capable of only σ bonding, $C_5H_{10}NH$. It is also worth noting that $Mo(CO)_5$(amine) compounds might be good starting reagents for obtaining other monosubstituted molybdenum carbonyls under very mild conditions.

---

(6) $Co(CO)_4SiCl_3$ was chosen for this experiment because of its thermal stability and because it has no infrared absorptions which overlap with those of $Mo(CO)_5C_5H_{10}NH$ or $Mo(CO)_6$.

(7) R. J. Angelici and B. E. Leach, *J. Organometal. Chem.* (Amsterdam), **11,** 203 (1968).

(8) J. R. Graham and R. J. Angelici, *J. Am. Chem. Soc.*, **87,** 5590 (1965).