

water as the composition of its inner-solvation shell varies.

The same point is disclosed, of course, in variation of the quantity $\bar{n}/(6 - \bar{n})r_a$ with solvent composition. Considering the data at 60°, this quantity has a value of 0.101 at $r_a = 0.288$ (the first experimental point), a maximum value of 0.115 at $r_a = 1.15$, gradually decreasing to a value of 0.040 at $r_a = 38.0$ (the last experimental point). With the ratio of activities of the solvent components as the relevant parameter, only a threefold variation in the discrimination toward water is exhibited by chromium(III). (As has already been pointed out, the variation is greater if the ratio of mole fractions is used.) A threefold variation is not large, being equivalent to only 0.73 kcal. mole⁻¹, and extensive speculation regarding the cause of this small trend is unwarranted. The decreasing tendency for chromium(III) to bind methanol as more methanol molecules are bound may be due to a steric repulsion of methanol molecules being *cis* to one another. The dimethanol species could be exclusively the *trans* isomer, thereby eliminating *cis* methanol-methanol interactions. However, such an assignment of configuration to the dimethanol species would make K_2 (cor.) = 0.76. Although this value is appreciably larger than K_1 (cor.), the corresponding difference in

value of ΔF° is only ~ 1.3 kcal. mole⁻¹, which could arise from mild differences of intramolecular interactions of ligands in the species and/or solvation energies of the species with $j = 0, 1, \text{ or } 2$.

Although the \bar{n} values may be slightly larger at 60°, the values of K_1 at 60 and 30° are within experimental error of one another and, therefore, $\Delta H_1 = 0 \pm 0.5$ kcal. mole⁻¹ and $\Delta S_1^\circ = -1.0 \pm 2$ cal. mole⁻¹ deg.⁻¹. The standard states chosen and the assumptions regarding activities of solvent components and ratios of activities coefficients of solvated chromium(III) ions makes this figure correspond to

$$\begin{aligned} & (\bar{S}^\circ_{\text{Cr}(\text{OH})_2\text{OHMe}^{3+}} - \bar{S}^\circ_{\text{Cr}(\text{OH})_2^{3+}}) + S^\circ_{\text{H}_2\text{O}} - S^\circ_{\text{MeOH}} \\ & \text{The value of } (S^\circ_{\text{H}_2\text{O}} - S^\circ_{\text{MeOH}}) \text{ is } -13.6 \text{ cal. mole}^{-1} \\ & \text{deg.}^{-1}, \text{ giving, therefore} \\ & \bar{S}^\circ_{\text{Cr}(\text{OH})_2\text{OHMe}^{3+}} - \bar{S}^\circ_{\text{Cr}(\text{OH})_2^{3+}} = \\ & \qquad \qquad \qquad +14 \pm 2 \text{ cal. mole}^{-1} \text{ deg.}^{-1} \end{aligned}$$

Of this 14 cal. mole⁻¹ deg.⁻¹, 3.6 cal. mole⁻¹ deg.⁻¹ ($R \ln 6$) is due to the lower symmetry of methanolpenta-aquochromium(III) ion relative to that of hexa-aquochromium(III) ion, and the remainder is due to unresolved contributions from differences of entropies of the two gaseous ions and differences of their entropies of solution.

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Carbon Monoxide Insertion Reactions. The Reaction of Methylmanganese Pentacarbonyl with Amines and Phosphines

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RECEIVED MAY 13, 1964

$\text{CH}_3\text{Mn}(\text{CO})_5$ was found to react with cyclohexylamine in ethers and in nitromethane to give $\text{CH}_3\text{COMn}(\text{CO})_4(\text{amine})$ at a rate which was first order in $\text{CH}_3\text{Mn}(\text{CO})_5$ but independent of the amine concentration. In methanol the rate was dependent on amine concentration but approached a limiting value at high concentrations. Similar results were obtained with triphenylphosphine and triphenyl phosphite. The reaction between $\text{CH}_3\text{Mn}(\text{CO})_5$ and N-methylcyclohexylamine in tetrahydrofuran did not go to completion, but the rate of approach to equilibrium was first order in $\text{CH}_3\text{Mn}(\text{CO})_5$. In *n*-hexane the reaction between $\text{CH}_3\text{Mn}(\text{CO})_5$ and cyclohexylamine was first order in both reactants. In mesitylene both a first-order path and a second-order path operated simultaneously. The results can all be explained by a unified mechanism involving the solvent-assisted dissociation common for nearly all octahedral complexes. Only when the coordinating ability of the solvent becomes extremely low does the nucleophilic reagent take over its role.

Introduction

Methylmanganese pentacarbonyl reacts with a variety of nucleophiles, L, to give products of the type $\text{CH}_3\text{COMn}(\text{CO})_4\text{L}$. Nucleophiles known to cause this reaction include carbon monoxide,¹ cyclohexylamine, N-methylcyclohexylamine, aniline, and ammonia.²

It has been shown³ that in the reaction with carbon monoxide, the entering molecule of carbon monoxide is not found in the acetyl group of the product.

This latter reaction has been shown⁴ to be first order in $\text{CH}_3\text{Mn}(\text{CO})_5$ and (in the range of carbon monoxide concentrations studied, which was severely limited by the solubility of the gas in the solvents used) first order

in carbon monoxide. The mechanism proposed by these authors for this reaction involved a direct attack on the $\text{CH}_3\text{Mn}(\text{CO})_5$ by CO, simultaneous with an intramolecular rearrangement to form the acetyl group.

We wished to discover whether this mechanism was general for the reactions of $\text{CH}_3\text{Mn}(\text{CO})_5$ with other nucleophiles, where the concentration range for the nucleophile was not so restricted as it is for carbon monoxide. The nucleophiles used were cyclohexylamine, N-methylcyclohexylamine, triphenylphosphine, triphenyl phosphite, and triphenylarsine.

It should be noted at this point that the stereochemistry of the complexes $\text{CH}_3\text{COMn}(\text{CO})_4\text{L}$ was not known at the start of this work, nor did we discover any really definite evidence as to whether the incoming ligand was *cis* or *trans* with respect to the acetyl group. We have, however, recently been informed⁵ that both isomers of the compound $\text{CH}_3\text{COMn}(\text{CO})_4\text{P}(\text{C}_6\text{H}_5)_3$

(1) T. H. Coffield, R. D. Closson, and J. Kozikowski, *J. Org. Chem.*, **22**, 598 (1957).

(2) K. A. Keblyns and A. H. Filbey, *J. Am. Chem. Soc.*, **82**, 4204 (1960).

(3) T. H. Coffield, *et al.*, Abstracts of Conference Papers, International Conference on Coordination Chemistry, London, April 6-11, 1959, Paper No. 26.

(4) F. Calderazzo and F. A. Cotton, *Inorg. Chem.*, **1**, 30 (1962).

(5) C. S. Kraihanzel, private communication.

have been isolated. Comparison of the conditions used shows that the compound formed in our experiments was the *cis* isomer.

Experimental

Preparation and Purification of Materials.— $\text{CH}_3\text{Mn}(\text{CO})_5$ was prepared as described in the literature,¹ using $\text{Mn}_2(\text{CO})_{10}$ which was a gift from the Ethyl Corporation.

Cyclohexylamine and *N*-methylcyclohexylamine were fractionally distilled before use. Triphenylphosphine and triphenylarsine were recrystallized from petroleum ether. Triphenyl phosphite (obtained from Eastman Kodak Co.) was used without further purification.

Methanol,⁶ tetrahydrofuran,² nitromethane,⁷ mesitylene,⁴ and bis(β -ethoxyethyl) ether⁴ were purified as described in the literature. Bis(β -methoxyethyl) ether was treated in the same way as its ethoxy analog. *n*-Hexane was dried over sodium wire and then fractionated.

Determination of Rates.—The reactions were followed by observing the increase of absorbance at 370 μ of 10^{-3} *M* solutions of $\text{CH}_3\text{Mn}(\text{CO})_5$ in the presence of varying concentrations (greater than 2×10^{-2} *M*) of nucleophile. $\text{CH}_3\text{Mn}(\text{CO})_5$ does not absorb light of this wave length appreciably, while the products $\text{CH}_3\text{COMn}(\text{CO})_4\text{L}$ absorb strongly.

A Beckman DK2 spectrophotometer was used for preliminary runs and for comparing final spectra with those of known samples of the products. A Beckman DU spectrophotometer was used for the remainder of the work. In two cases, reactions were followed by observing the rate of disappearance of the band at 5.03 μ in the infrared spectrum of $\text{CH}_3\text{Mn}(\text{CO})_5$. In these cases 1.25×10^{-2} *M* solutions of $\text{CH}_3\text{Mn}(\text{CO})_5$ were used, with nucleophile concentrations greater than 2.5×10^{-1} *M*. The rate constants obtained were in good agreement with those obtained by the other method. A Beckman IR5 spectrophotometer was used for these kinetic studies, and a Baird 4-55 spectrophotometer was used to record the spectra of the compounds prepared.

Product Identification.—The complex $\text{CH}_3\text{COMn}(\text{CO})_4(\text{C}_6\text{H}_{11}\text{NH}_2)$ was prepared by the method of Keblys and Filbey² and was found to melt at 97° (lit. m.p. 97°). The infrared spectrum of the complex in Nujol mull showed bands at the following wave lengths (μ): 4.85 (m), 5.04 (s), 5.13 (s), 5.20 (s), and 6.27. In carbon tetrachloride solution bands were observed at 4.88 (m), 5.00 (m), 5.10 (s), 5.19 (s), and 6.22 μ . This was in excellent agreement with a spectrum provided by Filbey,⁸ which showed bands at 4.86 (m), 5.00 (m), 5.11 (s), 5.20 (s), and 6.22 μ .

The compound $\text{CH}_3\text{COMn}(\text{CO})_4(\text{C}_6\text{H}_{11}\text{NHCH}_3)$ was also prepared by the method of Keblys² and melted at 73° (lit. m.p. 73–74°).

The new compound $\text{CH}_3\text{COMn}(\text{CO})_4\text{P}(\text{C}_6\text{H}_5)_3$ was prepared by treating a solution of $\text{CH}_3\text{Mn}(\text{CO})_5$ (0.2 g.) in tetrahydrofuran with a solution of triphenylphosphine (0.25 g.) in tetrahydrofuran, under nitrogen. After several hours of stirring, the solvent was evaporated *in vacuo* and the residual solid recrystallized from petroleum ether, yield 72%, m.p. 107°.

Anal. Calcd. for $\text{CH}_3\text{COMn}(\text{CO})_4\text{P}(\text{C}_6\text{H}_5)_3$: C, 61.0; H, 3.84; P, 6.56. Found: C, 61.4; H, 3.89; P, 6.53.

The infrared spectrum of this compound in Nujol mull was rather similar to that of the cyclohexylamine compound, showing bands at 4.86 (m), 5.04 (sh), 5.12 (s), 5.19 (sh), and 6.16 μ .

No solid product could be isolated from the reaction of $\text{CH}_3\text{Mn}(\text{CO})_5$ and triphenyl phosphite, but the fact that the changes in ultraviolet, visible, and infrared spectra during the reaction were similar to those for the reaction with triphenylphosphine is strong evidence for the formation of the complex $\text{CH}_3\text{COMn}(\text{CO})_4\text{P}(\text{OC}_6\text{H}_5)_3$.

No reaction was observed between $\text{CH}_3\text{Mn}(\text{CO})_5$ and triphenylarsine in tetrahydrofuran over a period of 24 hr.

Results

The reactions of $\text{CH}_3\text{Mn}(\text{CO})_5$ with cyclohexylamine, *N*-methylcyclohexylamine, triphenylphosphine, and triphenyl phosphite were all first order in $\text{CH}_3\text{Mn}(\text{CO})_5$ regardless of the solvent used. The observed first-order rate constants for these reactions are listed in Tables I,

II, and III. In addition, it was observed that the reaction in dimethylformamide of cyclohexylamine and $\text{CH}_3\text{Mn}(\text{CO})_5$ was too rapid to measure by our methods. In the case of *N*-methylcyclohexylamine the reactions did not go to completion, and the rate constants here refer to the rate of approach to the equilibrium position.

TABLE I
REACTION OF $\text{CH}_3\text{Mn}(\text{CO})_5$ WITH CYCLOHEXYLAMINE IN SOLVENTS IN WHICH THE RATE IS INDEPENDENT OF AMINE CONCENTRATION

| Solvent | Amine concn., mole/l. | Temp., °C. | $10^4 k_{\text{obsd.}}$, sec. ⁻¹ |
|-----------------------------------------------|-----------------------|------------|----------------------------------------------|
| Bis(β -ethoxyethyl) ether ^a | 0.0540 | 25.5 | 3.66 |
| | 0.1240 | 25.5 | 3.64 |
| | 0.4670 | 25.5 | 3.77 |
| | 0.0513 | 19.3 | 2.14 |
| | 0.0575 | 12.2 | 0.941 |
| Tetrahydrofuran ^b | 0.0283 | 25.5 | 9.08 |
| | 0.0647 | 25.5 | 9.31 |
| | 0.1130 | 25.5 | 9.72 |
| | 0.1400 | 25.5 | 9.75 |
| | 0.4710 ^c | 25.5 | 10.3 |
| | 0.0696 | 34.9 | 20.5 |
| | 0.0710 | 21.2 | 5.76 |
| Bis(β -methoxyethyl) ether | 0.0440 | 25.5 | 11.4 |
| | 0.0699 | 25.5 | 11.7 |
| Nitromethane | 0.0369 | 25.5 | 16.6 |
| | 0.0870 | 25.5 | 16.5 |

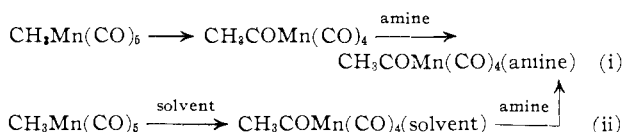
^a $E_a = 17.5$ kcal./mole. ^b $E_a = 17.2$ kcal./mole. ^c Based on the rate of disappearance of the band at 5.03 μ in the infrared spectrum of methylmanganese pentacarbonyl.

TABLE II
REACTION OF $\text{CH}_3\text{Mn}(\text{CO})_5$ WITH CYCLOHEXYLAMINE IN SOLVENTS IN WHICH THE RATE IS DEPENDENT ON AMINE CONCENTRATION^a

| Solvent | Amine concn., mole/l. | $10^4 k_{\text{obsd.}}$, sec. ⁻¹ |
|------------------|-----------------------|----------------------------------------------|
| Methanol | 0.0195 | 16.7 |
| | 0.0423 | 26.1 |
| | 0.0699 | 35.3 |
| | 0.1112 | 42.5 |
| | 0.1565 | 46.3 |
| Mesitylene | 0.0284 | 0.0540 |
| | 0.0500 | 0.0825 |
| | 0.0971 | 0.131 |
| <i>n</i> -Hexane | 0.1620 | 0.205 |
| | 0.0510 | 0.0103 |
| | 0.0896 | 0.0207 |
| | 0.1630 | 0.0404 |

^a All reactions performed at 25.5°

Reactions with Cyclohexylamine.—The results listed in Table I show that the rate of the reaction between $\text{CH}_3\text{Mn}(\text{CO})_5$ and cyclohexylamine was virtually independent of amine concentration in bis(β -ethoxyethyl) ether, tetrahydrofuran, bis(β -methoxyethyl) ether, and nitromethane. This ruled out a mechanism similar to that proposed by Calderazzo and Cotton⁴ for the reaction with carbon monoxide. Two possible mechanisms, which lead to the same rate expression, are

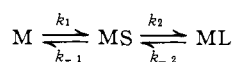


(6) N. Bjerrum and L. Zechmeister, *Ber.*, **56**, 894 (1923).

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

(8) A. H. Filbey, private communication.

Writing the reaction as



where M is the starting material, MS the intermediate (not necessarily solvated), and ML the final product,

TABLE III

REACTION OF $\text{CH}_3\text{Mn}(\text{CO})_5$ WITH (a) $\text{P}(\text{C}_6\text{H}_5)_3$, (b) $\text{P}(\text{OC}_2\text{H}_5)_3$, AND (c) N-METHYLCYCLOHEXYLAMINE^a

| Solvent | Ligand concn., mole/l. | $10^4 k_{\text{obsd.}}$ sec. ⁻¹ |
|----------------------------------|---------------------------|-----------------------------------------------|
| Tetrahydrofuran | (a) 0.0247 | 7.44 |
| | 0.0444 | 8.12 |
| | 0.3900 | 8.86 |
| Bis(β -ethoxyethyl) ether | (a) 0.0319 | 4.00 |
| | 0.0845 | 4.08 |
| Tetrahydrofuran | (b) 0.0218 | 3.70 |
| | 0.0343 | 4.80 |
| | 0.1210 | 7.50 |
| | 0.3090 | 8.96 |
| | 0.5340 ^b | 9.29 |
| Tetrahydrofuran | (c) 0.0340 | 15.5 |
| | 0.0396 | 14.3 |
| | 0.0607 | 11.3 |
| | 0.0780 | 10.3 |
| | 0.1107 | 9.36 |
| | 0.3590 | 8.35 |
| | 0.5240 | 8.16 |

^a All reactions performed at 25.5°. ^b Based on the rate of disappearance of the band at 5.03 μ in the infrared spectrum of $\text{CH}_3\text{Mn}(\text{CO})_5$.

and using the steady-state approximation for the concentration of the intermediate, one obtains the expression

$$\frac{d[\text{ML}]}{dt} = k_2[\text{L}] \frac{k_1[\text{M}] + k_{-2}[\text{ML}]}{k_{-1} + k_2[\text{L}]} - k_{-2}[\text{ML}] \quad (1)$$

for the rate of product formation. When k_2 is much larger than k_{-1} , this reduces to

$$\frac{d[\text{ML}]}{dt} = k_1[\text{M}]$$

in agreement with the results obtained in these four solvents. The independence of amine concentration means, in fact, that virtually all the intermediate reacts with the amine rather than reverting to the starting material. In these cases the observed rate constants, k_{obsd} , can be equated to k_1 , the rate constant for the formation of the intermediate from the starting material. However, if the rate constant for the reversion to starting material, k_{-1} , becomes comparable in size to the rate constant for the reaction with amine, k_2 , there will be a competition for the intermediate, which will result in a dependence of the observed rate constant on amine concentration. This appeared to be the case when the reaction was performed in methanol (see Table II). The observed rate constants, when plotted against amine concentration, rose toward a limiting value, as shown in Fig. 1.

If one simplifies eq. 1 by ignoring k_{-2} (a reasonable assumption since the reaction appeared to go to completion over the range of amine concentrations used), one obtains

$$\frac{d[\text{ML}]}{dt} = k_1 k_2 \frac{[\text{M}][\text{L}]}{k_{-1} + k_2[\text{L}]} \quad (2)$$

or

$$\frac{1}{k_{\text{obsd}}} = \frac{k_{-1}}{k_1 k_2} \left(\frac{1}{[\text{L}]} \right) + \frac{1}{k_1} \quad (3)$$

In agreement with eq. 3, a straight line was obtained on plotting $1/k_{\text{obsd}}$ against $1/[\text{L}]$ for the reactions in methanol. From this group (Fig. 2) values of 6.33×10^{-3} sec.⁻¹ for k_1 and 5.43×10^{-2} mole/l. for k_{-1}/k_2 were obtained.

It seemed probable that if the solvent played an important part in the formation of the intermediate, then the use of a nonpolar solvent might seriously hinder this mechanism. Table II and Fig. 3 show that the use of mesitylene and *n*-hexane as solvents resulted in a linear increase of observed rate constant with amine concentration. The values obtained for the second-order constant, k_2 , were: in mesitylene, 1.11×10^{-4} M⁻¹ sec.⁻¹; and in *n*-hexane, 2.7×10^{-5} M⁻¹ sec.⁻¹. Evidently the solvent still plays some part in the reaction, since the rate constant is four times larger in mesitylene than in *n*-hexane. In the case of mesitylene, the intercept of 2.18×10^{-6} sec.⁻¹ at zero amine concentration presumably represents k_1 for the amine-independent mechanism which predominates in the more polar solvents. The small negative intercept at zero amine concentration in *n*-hexane is probably the result of inaccuracy caused by some decomposition of the product during the very slow reaction.

Reactions with Other Nucleophiles. A.—Triphenylphosphine reacted with $\text{CH}_3\text{Mn}(\text{CO})_5$ in bis(β -ethoxyethyl) ether at a rate which was independent of ligand concentration and similar to that for cyclohexylamine, as would be expected since the nucleophile is not involved in the rate-determining step. In tetrahydrofuran the condition that k_2 should be much larger than k_{-1} did not appear to be fulfilled, as the rate constant increased slightly with ligand concentration. A plot of $1/k_{\text{obsd}}$ against $1/[\text{L}]$ gave a value of 9.00×10^{-4} sec.⁻¹ for k_1 , in reasonable agreement with that obtained for cyclohexylamine, and 5.09×10^{-3} mole/l. for k_{-1}/k_2 .

B.—The observed rate constants for the reaction between $\text{CH}_3\text{Mn}(\text{CO})_5$ and triphenyl phosphite increased with increasing phosphite concentration toward a limiting value, as shown in Fig. 4. This behavior was similar to, but more marked than, the behavior of triphenylphosphine in this solvent. In both cases this is presumably due to a competition between the reaction of the intermediate with the nucleophile and the reversion of the intermediate to the starting material. A plot of $1/k_{\text{obsd}}$ against $1/[\text{L}]$ (Fig. 5) gave a straight line, and from this values of 9.90×10^{-4} sec.⁻¹ for k_1 (again in reasonable agreement with the value for cyclohexylamine in the same solvent) and 3.65×10^{-2} mole/l. for k_{-1}/k_2 were obtained.

C.—The reaction of N-methylcyclohexylamine and $\text{CH}_3\text{Mn}(\text{CO})_5$ did not go to completion over the range of amine concentrations used. The approach to equilibrium was first order in $\text{CH}_3\text{Mn}(\text{CO})_5$, and the observed rate constant varied with ligand concentration.

Equation 1 can be integrated, giving the expression (where $[\text{ML}_{\text{eq}}]$ represents the concentration of product at equilibrium)

$$\ln ([ML_{eq}] - [ML]) = \ln [ML_{eq}] - \frac{k_{-1}k_{-2} + k_2k_1[L]}{k_{-1} + k_2[L]} t \quad (4)$$

which predicts an approach to equilibrium which is first order in $\text{CH}_3\text{Mn}(\text{CO})_5$, in agreement with our results. The observed rate constant is given by

$$k_{\text{obsd}} = \frac{k_{-1}k_{-2} + k_2k_1[L]}{k_{-1} + k_2[L]} \quad (5)$$

Equation 5 fits the data for variation of the amine concentration within experimental error. The observed constant should approach k_1 at very large amine concentrations. From direct spectrophotometric observation of the position of equilibrium in several runs, a mean equilibrium constant was obtained.

$$K = \frac{k_1k_2}{k_{-1}k_{-2}} = \frac{[\text{CH}_3\text{COMn}(\text{CO})_4(\text{amine})]}{[\text{CH}_3\text{Mn}(\text{CO})_5][\text{amine}]} = 23.8 \pm 1.4 \text{ l./mole}$$

Discussion

There appear to be two main points of interest raised by the results obtained in this work. One concerns the exact nature of the first step of the reaction and of the intermediate. The other is the comparison of the mechanism of this reaction with that of others, such as the reaction of $\text{CH}_3\text{Mn}(\text{CO})_5$ with CO, the reaction of the manganese pentacarbonyl halides with similar ligands, and indeed the substitution reaction of other low-spin d^6 octahedral metal complexes.

Table IV contains the rate constants for the first step

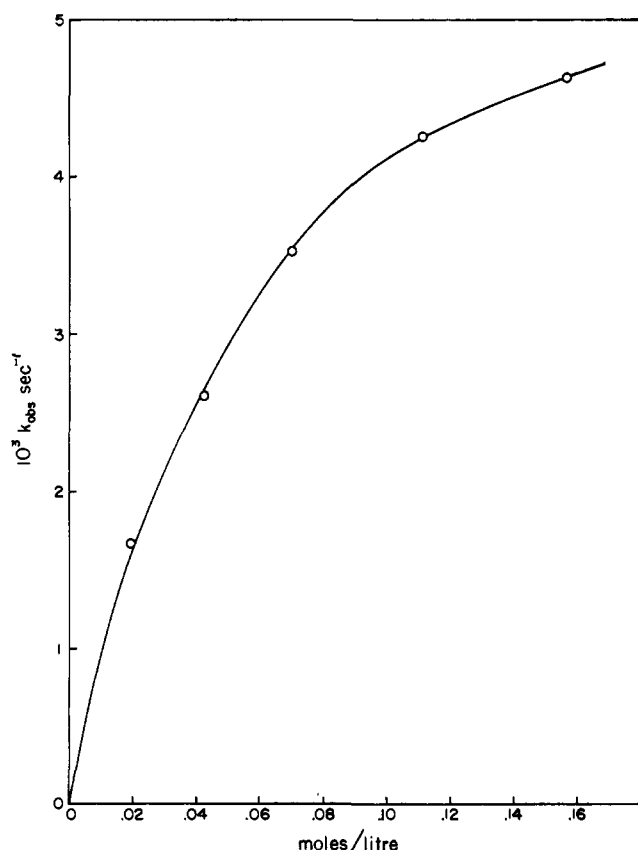


Fig. 1.—Plot of the observed rate constant vs. amine concentration for the reaction of $\text{CH}_3\text{Mn}(\text{CO})_5$ with cyclohexylamine in methanol.

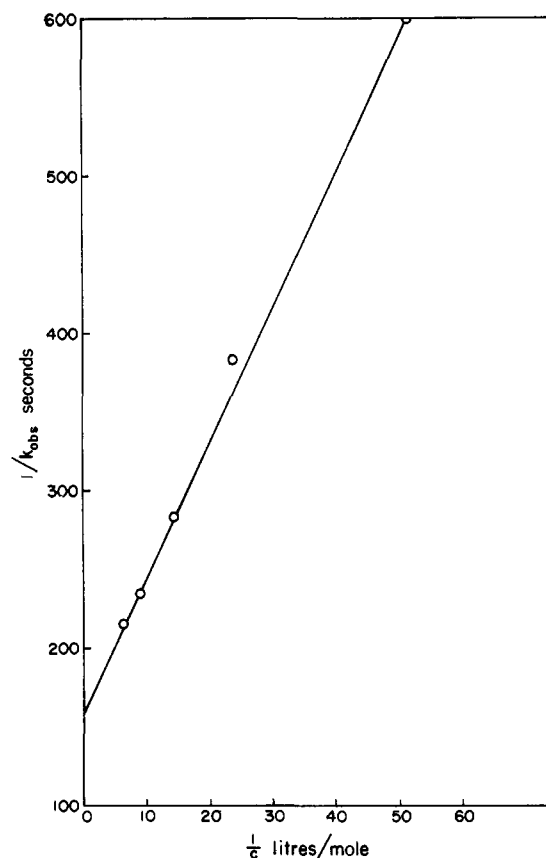


Fig. 2.—Plot of the reciprocal of observed rate constant vs. the reciprocal of amine concentration for the reaction of $\text{CH}_3\text{Mn}(\text{CO})_5$ with cyclohexylamine in methanol.

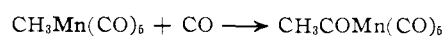
of the reaction between $\text{CH}_3\text{Mn}(\text{CO})_5$ and cyclohexylamine in the solvents used. Comparison of these rate constants with the dielectric constants of the sol-

TABLE IV
RATE CONSTANTS FOR THE FORMATION OF THE INTERMEDIATE FROM $\text{CH}_3\text{Mn}(\text{CO})_5^a$

| Solvent or nucleophile | $k_1, \text{sec.}^{-1}$ | $k_2, M^{-1} \text{sec.}^{-1}$ | Dielectric constant |
|-----------------------------------|-------------------------|--------------------------------|---------------------|
| Dimethylformamide | $>1.50 \times 10^{-2}$ | $>1.00 \times 10^{-3}$ | 26.6 (25°) |
| Methanol | 6.33×10^{-3} | 2.56×10^{-4} | 31.2 (20°) |
| Nitromethane | 1.66×10^{-3} | 8.94×10^{-6} | 37.4 (20°) |
| Bis(β -methoxyethyl) ether | 1.16×10^{-3} | 1.63×10^{-4} | ? |
| Tetrahydrofuran | 9.63×10^{-4} | 7.88×10^{-6} | 7.70 (25°) |
| Bis(β -ethoxyethyl) ether | 3.69×10^{-4} | 6.60×10^{-6} | 5.68 (25°) |
| Mesitylene | 2.18×10^{-6} | 3.03×10^{-7} | 2.27 (20°) |
| <i>n</i> -Hexane | ... | ... | 1.91 (20°) |
| Cyclohexylamine ^b | ... | 1.11×10^{-4} | |
| Cyclohexylamine ^c | ... | 2.70×10^{-5} | |

^a All rate constants refer to the reaction with cyclohexylamine at 25.5°. ^b In mesitylene. ^c In *n*-hexane.

vents shows that, in general, a more polar solvent aids the reaction. This could be taken as evidence that the function of the solvent is merely to ease the charge separation which occurs during the rearrangement to form the acetyl group. This is the type of explanation given earlier⁴ to account for the variation in rate of the reaction



with the dielectric constant of the solvent.

However, the fact that k_1 is considerably larger for

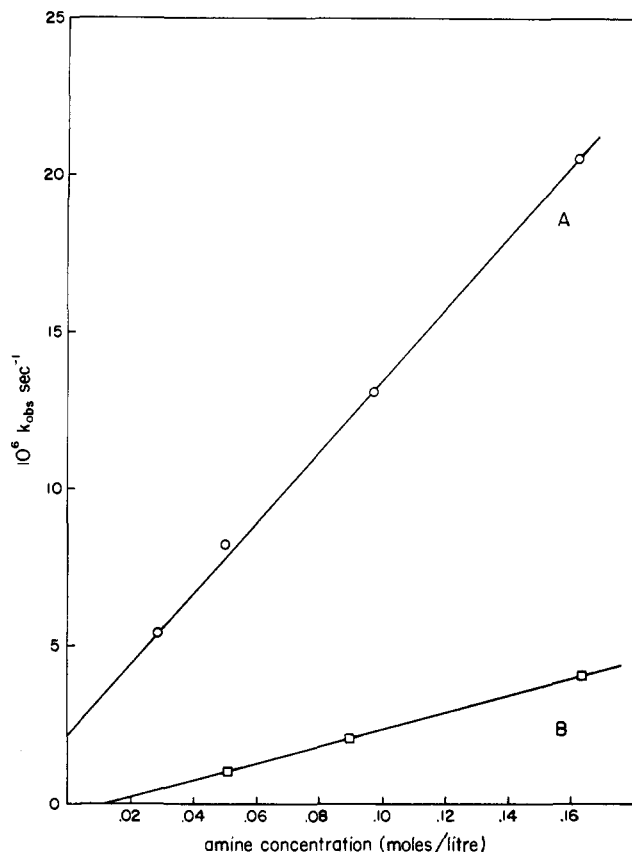
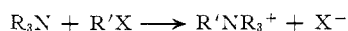


Fig. 3.—Plot of the observed rate constant vs. amine concentration for the reaction of $\text{CH}_3\text{Mn}(\text{CO})_5$ with cyclohexylamine in (A) mesitylene and (B) *n*-hexane.

methanol than for nitromethane, although the latter has the higher dielectric constant, suggests that the coordinating ability of the solvent may also be important. Furthermore, an examination of data in the literature⁹ for the effects of solvents on the rates of reactions where large changes in polarity occur shows that these effects are relatively small. For example, in the reaction of amines and alkyl halides to form quaternary ammonium salts



the transition state must certainly be considerably more polar than the reactants, and yet the effect of changing the solvent over a range from methyl alcohol to mesitylene is only a factor of 100 or less on the rate.⁹

In Table IV we have computed second-order rate constants from the first-order rate constants in different solvents by simply dividing by the "concentration" of the solvent (weight of 1 l. of the solvent divided by its molecular weight). The numbers may be compared with the second-order rate constants for cyclohexylamine in mesitylene and *n*-hexane. The rate constants obtained cover a range of 10^3 – 10^4 , which is probably too large for a simple polarity effect and suggests that the coordinating ability, or nucleophilic power, of the solvent plays some part.

If the literature is examined¹⁰ for the effect of different nucleophilic reagents on the rates of reactions where a bimolecular displacement mechanism seems established, variations in rate constants of 10^6 to 10^{12}

(9) R. G. Pearson, *J. Chem. Phys.*, **20**, 1478 (1952).

(10) J. O. Edwards and R. G. Pearson, *J. Am. Chem. Soc.*, **84**, 16 (1962).

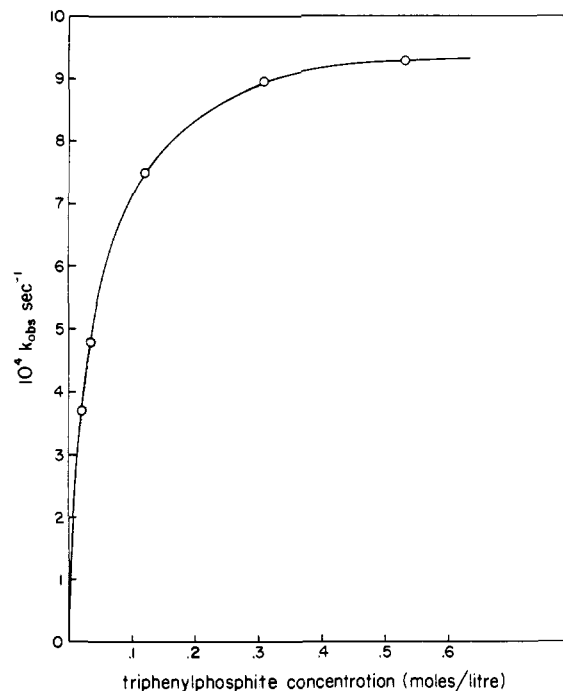


Fig. 4.—Plot of the observed rate constant vs. phosphite concentration for the reaction of $\text{CH}_3\text{Mn}(\text{CO})_5$ with triphenyl phosphite in tetrahydrofuran.

for various substrates are found. By comparison, then, the reaction of $\text{CH}_3\text{Mn}(\text{CO})_5$ with different nucleophiles shows only a modest dependence on the properties of the nucleophile.

The simplest explanation would seem to be that the mechanism is a solvent-assisted migration very closely related to the solvent-assisted dissociation mechanism that has been suggested for many other octahedral complexes.¹¹ A detailed discussion would suppose that the breaking of the manganese–methyl bond is the critical step of the reaction process.¹²

The breaking of this bond would be facilitated by the partial formation of a bond by the methyl group to an adjacent carbonyl. The complete migration would not occur until a solvent molecule (or other new ligand) entered the coordination sphere. This would eliminate the need to form a high energy intermediate of reduced coordination number. The solvated intermediate must also be unstable since, in the absence of a nucleophile, there is no good evidence that any solvated species is formed.

It would be surprising if the reaction of $\text{CH}_3\text{Mn}(\text{CO})_5$ with CO had a different mechanism from that for the nucleophiles used here. Accordingly, we examined the possibility that a common mechanism could apply to both reactions. It is interesting to note that the rate equation (2) can be simplified to

$$\frac{d[\text{ML}]}{dt} = \frac{k_1 k_2}{k_{-1}} [\text{M}][\text{L}] \quad (6)$$

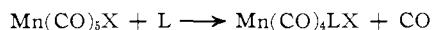
when $[\text{L}]$ is small enough to make $k_2[\text{L}]$ much smaller than k_{-1} . Since the low solubility of carbon monoxide

(11) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 98 ff.; T. P. Jones, W. E. Harris, and W. J. Wallace, *Can. J. Chem.*, **39**, 2371 (1961); R. G. Pearson and R. D. Lanier, *J. Am. Chem. Soc.*, **86**, 765 (1964).

(12) It is not yet established that the reaction involves migration of a methyl group rather than a carbonyl group. However, the methyl migration seems much more likely.

in the solvents used automatically keeps $[L]$ small, the first-order dependence on carbon monoxide concentration⁴ in bis(β -ethoxyethyl) ether does not rule out the possibility that this reaction has the same mechanism as the reaction of $\text{CH}_3\text{Mn}(\text{CO})_5$ with other nucleophiles. In any event, a comparison of the observed second-order rate constants for the reaction in mesitylene of $\text{CH}_3\text{Mn}(\text{CO})_5$ with CO ($4.49 \times 10^{-4} M^{-1} \text{sec.}^{-1}$ at 30°) and with cyclohexylamine ($1.11 \times 10^{-4} M^{-1} \text{sec.}^{-1}$ at 25°) shows that even when the rate is dependent on the concentration of the nucleophile, it is not greatly affected by a change in the nature of the nucleophile.

The reactions of manganese pentacarbonyl halides with a variety of ligands have been studied by Angelici and Basolo.⁷ As in the case of $\text{CH}_3\text{Mn}(\text{CO})_5$, the rate



of reaction was found to be independent of the nature and concentration of the ligand used, which caused the authors to suggest that the rate-determining step involved the loss of carbon monoxide to form an intermediate of lower coordination number. Since the reaction proceeded smoothly in nonpolar solvents, it was virtually certain that solvent did not become coordinated in the rate-determining step. The effect of changing the solvent on the rate of the reaction was far smaller than for the reactions of $\text{CH}_3\text{Mn}(\text{CO})_5$ and

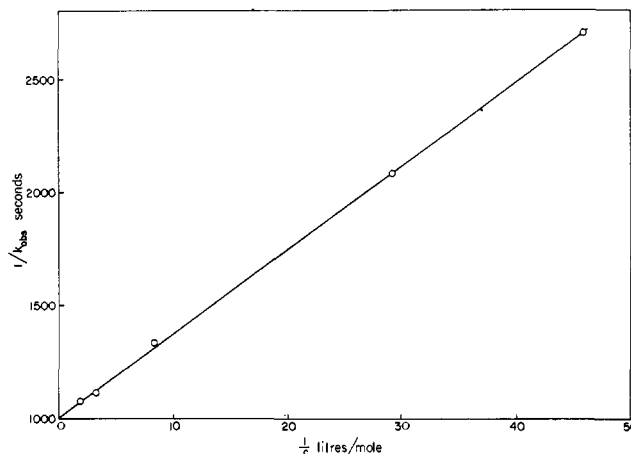


Fig. 5.—Plot of the reciprocal of observed rate constant vs. the reciprocal of phosphite concentration for the reaction of $\text{CH}_3\text{Mn}(\text{CO})_5$ with triphenyl phosphite in tetrahydrofuran.

was in the reverse direction; that is, the more polar solvents slowed the reaction down. This is in agreement with a transition state which is slightly less polar than the starting material, in contrast to the more polar transition state in the reactions of $\text{CH}_3\text{Mn}(\text{CO})_5$.

Acknowledgments.—This research was supported in part by the U. S. Atomic Energy Commission under Contract At(11-1)-1087 and in part by the National Science Foundation (GP-1471).

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Studies on Nickel(II) Complexes. VII. A Nuclear Resonance Investigation of Mixed Ligand Complexes

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RECEIVED JUNE 8, 1964

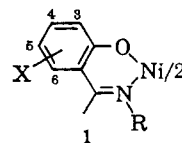
Equilibration of solutions of differently substituted bis(salicylaldimine)-Ni(II) complexes which are involved in a planar \rightleftharpoons tetrahedral conformational equilibrium results in rapid and nearly statistical ligand exchange. The mixed ligand complexes thus produced have been unambiguously identified by their proton resonance spectra which, like those of the pure complexes, exhibit characteristic isotropic proton hyperfine contact interactions. Spin densities in the mixed complexes have been measured, and comparison with the pure complexes shows that an asymmetric redistribution of spin has occurred. A recent model for the production of asymmetric spin density distributions is applied to the mixed salicylaldimine complexes. A probable mechanism for the ligand-exchange process is discussed.

Introduction

As part of a continuing series of investigations in these laboratories concerning the solution equilibria of bis(chelate)nickel(II) complexes,²⁻⁷ we have discovered facile ligand-exchange reactions between variously substituted bis(salicylaldimine) complexes of general type 1. These exchange reactions take place rapidly in solution in the absence of any added free ligand.

- (1) Alfred P. Sloan Foundation Fellow.
- (2) Part V: R. H. Holm, A. Chakravorty, and G. O. Dudek, *J. Am. Chem. Soc.*, **86**, 379 (1964).
- (3) Part VI: A. Chakravorty and R. H. Holm, *Inorg. Chem.*, **3**, 1010 (1964).
- (4) (a) R. H. Holm and K. Swaminathan, *ibid.*, **2**, 181 (1963); see also (b) L. Sacconi, P. Paoletti, and M. Ciampolini, *J. Am. Chem. Soc.*, **85**, 411 (1963); L. Sacconi, M. Ciampolini, and N. Nardi, *ibid.*, **86**, 819 (1964).
- (5) R. H. Holm, A. Chakravorty, and G. O. Dudek, *ibid.*, **85**, 821 (1963).
- (6) (a) R. H. Holm and K. Swaminathan, *Inorg. Chem.*, **1**, 599 (1962); see also (b) L. Sacconi and M. Ciampolini, *J. Am. Chem. Soc.*, **85**, 1750 (1963); (c) E. A. LaLancette, D. R. Eaton, R. E. Benson, and W. D. Phillips, *ibid.*, **84**, 3968 (1962).
- (7) R. H. Holm, *ibid.*, **83**, 4683 (1961).

The mixed ligand complexes thus produced can be readily detected from measurements of their isotropic



proton hyperfine contact shifts,⁸ which are in most cases distinguishable from the contact shifts of the unmixed complexes, the spectra of which are unchanged. The utilization of the contact shift technique for the study of the mixed ligand complexes necessitates that at least a fraction of the unmixed and mixed complexes exist in a paramagnetic configuration. Accordingly, the complexes studied in this work have $R = \text{sec-alkyl}$ and/or $t\text{-butyl}$ groups. It has been previously demon-

- (8) D. R. Eaton, A. D. Josey, W. D. Phillips, and R. E. Benson, *J. Chem. Phys.*, **37**, 347 (1962).