H, 3.4; B, 33.9; N, 7.7; Cl, 42.7. Ultraviolet $\lambda_{\max}^{\mathrm{CH_3CN}}$ 247 mμ (ϵ 53,500).

(**B**).—Oxalyl chloride (4 ml., 41 mmoles) was added to a mixture of $(CH_3)_2SB_{10}H_7COOH \cdot N_2$ (5 g., 20 mmoles) and 60 ml. of acetonitrile. The mixture was refluxed 7 hr., cooled, and sodium azide (2 g., 62 mmoles) was added. The mixture was stirred overnight, during which time 800 ml. of gas (32.8 mmoles) was evolved. The solution was stirred into 700 ml. of water to precipitate 5.2 g. of a dark brown solid. Infrared analysis suggested this was $(CH_3)_2SB_{10}H_7NCO \cdot N_2$, but it was not obtained in analytically pure form. Glyme (50 ml.) and 4.2 g. of the crude isocyanate were mixed with 10 ml. of 12 *M* hydrochloric acid. Virtually all the solid dissolved and remained in solution during the addition of two more 10-ml. portions of 12 *M* hydrochloric acid. During the additions the dark solution became hot and gas was evolved. It was concentrated to 30 ml. on a steam bath, 45 ml. of water was added, and the solution was filtered through "Celite" filter aid. Mixing an aliquot with hydrated $H_2B_{12}Cl_{12}$ precipitated $[(CH_3)_2SB_{10}H_7NH_3 \cdot N_2^+]_2B_{12}Cl_{12}$, identical by infrared analysis with that prepared above. The major part of the solution was made alkaline with sodium hydroxide. $(CH_3)_2SB_{10}H_7NH_2 \cdot N_2$ precipitated and was recrystallized from water, dec. pt. 105–107°. *Anal.* Calcd. for $(CH_3)_2SB_{10}H_7NH_2 \cdot N_2$: C, 10.8; H, 6.8; B, 48.9; N, 19.0. Found: C, 11.5; H, 7.0; B, 48.9; N, 18.2. Ultraviolet $\lambda_{\max}^{\mathrm{CH_3CN}}$ 255 mμ (ϵ 25,000).

(**C**).—Sodium azide was added to a solution of $(CH_3)_2SB_{10}H_7COOH \cdot N_2$ in concentrated aqueous $H_2B_{12}Cl_{12}$. Gassing ensued and $[(CH_3)_2SB_{10}H_7NH_3 \cdot N_2^+]_2B_{12}Cl_{12}^{2-}$, identified by infrared analysis, separated.

CONTRIBUTION FROM CYANAMID EUROPEAN RESEARCH INSTITUTE,
COLOGNY, GENEVA, SWITZERLAND

The Manganese-Catalyzed Carbonylation of Amines

BY F. CALDERAZZO

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Decacarbonyldimanganese and pentacarbonylmethylmanganese have been found to catalyze the carbonylation of primary aliphatic amines almost exclusively to 1,3-dialkylureas. Ammonia and di-*n*-butylamine virtually do not react. Aniline reacts very slowly giving 1,3-diphenylurea in low yield. The formation of 1,3-dialkylureas is accompanied by the evolution of hydrogen, so that little or no gas absorption was observed during the reaction. A mechanism of reaction is proposed involving the attack of the amine on an alkylformamide group bonded to the manganese. A simplified procedure for the preparation of decacarbonyldimanganese is also described.

Introduction

Kinetic data concerning the reaction of pentacarbonylalkylmanganese compounds with nucleophilic reagents have been previously reported[1,2] in the case of L = carbon monoxide.

$$RMn(CO)_5 + L \longrightarrow RCOMn(CO)_4L \qquad (1)$$

Kinetic studies of the reaction of $CH_3COMn(CO)_5$ with phosphorus- and nitrogen-containing ligands

$$CH_3COMn(CO)_5 + L \longrightarrow CO + CH_3COMn(CO)_4L \qquad (2)$$

are now being completed and the results will be reported later.

The present paper reports some catalytic reactions in which primary aliphatic amines can be converted into disubstituted ureas by the use of decacarbonyldimanganese and pentacarbonylmethylmanganese as catalytic precursors. This study was originated by the observation of some anomalies found during the kinetic investigation of reaction 2 with L = amines. Catalytic carbonylations of primary, secondary, and tertiary amines are known to occur in the presence of group VIII metal carbonyls or of metal halides capable of being transformed to metal carbonyls in the reaction conditions.[3-9] Alkylformamides are usually obtained in the course of these reactions, although dialkylureas are also reported[5] to be formed when large amounts of nickel iodide are employed. Aniline appears to be unique in giving almost exclusively diphenylurea.[5,6] Finally, diphenylurea was the main by-product during the reaction of aniline, carbon monoxide, and olefins to give anilides using $Co_2(CO)_8$ as catalyst.[10]

The catalytic properties of decacarbonyldimanganese and related compounds in the carbonylation reactions of amines do not appear to have been investigated. It has now been found that $Mn_2(CO)_{10}$ and $CH_3Mn(CO)_5$ catalyze the reaction. Moreover, manganese seems to differ from the above-mentioned metals since primary aliphatic amines react giving almost exclusively dialkylureas and secondary aliphatic amines are virtually unreacted. Other interesting features of the manganese system will be discussed later in the text.

Experimental

(1) **Materials.**—Tetrahydrofuran and diisopropyl ether were dried over sodium, distilled over $LiAlH_4$, and stored under nitrogen. *n*-Butylamine and cyclohexylamine were dried over KOH pellets and fractionated. Aniline was distilled and stored under nitrogen. Di- and tri-*n*-butylamine were fractionated under reduced pressure. Anhydrous manganese(II) acetate was prepared by drying the commercially available hydrate product over P_2O_5 at room temperature for several days under high vacuum.

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TABLE I

CARBONYLATION OF AMINES IN THE PRESENCE OF $Mn_2(CO)_{10}$ AND $CH_3Mn(CO)_5$[c]

Run no.	Amine	Solvent	Mn, g.-atom/l.	Temp., °C.	Reaction time, hr.	Yield[a]	
						1,3-Dialkylurea	N-Alkylformamide
1	Cyclohexylamine	Heptane	$Mn_2(CO)_{10}$; 0.046	180–200	12	41	3
2	Cyclohexylamine	Heptane	$CH_3Mn(CO)_5$; 0.013	180–190	12	25	Low[d]
3	Cyclohexylamine	THF[b]	$Mn_2(CO)_{10}$; 0.044	180–200	12	58	N.d.
4	Cyclohexylamine	. . .	$Mn(CH_3COO)_2$; 0.046	170–180	20	. . .	4
5	*n*-Butylamine	. . .	$Mn_2(CO)_{10}$; 0.046	180	12	52	Low[d]
6	*n*-Butylamine	Heptane	$Mn_2(CO)_{10}$; 0.046	180–200	12	47	7
7	*n*-Butylamine	. . .	. . .	180–200	23	. . .	4
8	*n*-Butylamine	Heptane	$Mn_2(CO)_{10}$; 0.044	120–130	35	15	Low[d]
9	*n*-Butylamine	THF	$CH_3Mn(CO)_5$; 0.013	180–200	12	33	7
10	Aniline	THF	$CH_3Mn(CO)_5$; 0.019	180–250	20	. . .	. . .
11	Aniline	Heptane	$Mn_2(CO)_{10}$; 0.046	190	48	6	. . .
12	Di-*n*-butylamine	. . .	$Mn_2(CO)_{10}$; 0.047	180–190	20	. . .	3
13	Di-*n*-butylamine	THF[b]	$CH_3Mn(CO)_5$; 0.013	140	14	. . .	Low[d]
14	Tri-*n*-butylamine	. . .	$Mn_2(CO)_{10}$; 0.048	180–200	11	. . .	. . .
15	Ammonia	Heptane	$Mn_2(CO)_{10}$; 0.046	180–190	20	. . .	. . .
16	Ammonia	THF[b]	$CH_3Mn(CO)_5$; 0.0129	150–180	20	Low[d]	. . .

[a] Molar conversion of amine. [b] THF = tetrahydrofuran. [c] Initial CO pressures ranged from 106 to 135 atm., with one exception where the pressure was 87 atm. (run 13). [d] Between 1 and 3%.

Pentacarbonylmethylmanganese was prepared from $NaMn(CO)_5$ and dimethyl sulfate in diethyl ether according to Closson, Kozikowski, and Coffield.[11]

Hydrogen was detected by gas chromatography on a Perkin-Elmer Model 116 vapor fractometer with a type I column at about 25°.

Microanalyses are by Dr. K. Eder, Ecole de Chimie, Geneva, Switzerland.

(2) **Preparation of Decacarbonyldimanganese.**—The carbonyl was prepared by a simplified procedure described[12] by Podall, Dunn, and Shapiro. Triisobutylaluminum (210 ml.) dissolved under nitrogen in 200 ml. of diisopropyl ether was introduced rapidly into a 1-l. stainless-steel autoclave containing 35 g. of anhydrous manganese(II) acetate suspended in 150 ml. of diisopropyl ether. Carbon monoxide (125 atm.) was compressed in the autoclave and the mixture was stirred and heated gradually up to 60° during 3 hr. At this temperature gas absorption took place. The temperature was raised to 140° and maintained at this level for 20 hr. After cooling, the gas was vented and the orange-brown solution containing crystalline $Mn_2(CO)_{10}$ in suspension was collected under nitrogen, cooled at about −50°, and filtered. By sublimation at 50° (0.1 mm.) the carbonyl was obtained in a pure state (19.1 g., 48% yield).

(3) **Carbonylations of Amines.**—The carbonylations of amines were carried out in a magnetically-stirred 500-ml. stainless steel autoclave. Particular care was taken to purify carbon monoxide from $Fe(CO)_5$ present in commercially available gas. Preliminary experiments with unpurified commercial carbon monoxide gave completely erratic results. The gas was purified by shaking under pressure with a solution of iodine in 2,2′-diethoxydiethyl ether.

(a) **Carbonylation of Cyclohexylamine (Run 1 in Table I).**—Cyclohexylamine (132 g., 153 ml., 1.33 moles) and heptane (100 ml.) were placed in the autoclave together with $Mn_2(CO)_{10}$ (2.26 g.). Carbon monoxide was compressed up to 130 atm. and the content of the autoclave stirred and heated at 180–200° for 12 hr. After cooling, no significant gas absorption was observed. Hydrogen was present in the gas phase, as detected by gas chromatography. The colorless, crystalline dicyclohexylurea suspended in the reaction medium was collected under nitrogen, filtered, washed with heptane, and dried *in vacuo* (60.8 g., 40.7% yield based on the starting amine). The dicyclohexylurea so prepared had m.p. 230–234°. Mixed with an authentic sample of 1,3-dicyclohexylurea (m.p. 233–234.5°, lit.[13] 229–230°) prepared from $COCl_2$ and cyclohexylamine, the m.p. was 231.5–234°. After crystallization from ethyl alcohol, m.p. 232–234°.

Anal. Calcd. for $C_{13}H_{24}N_2O$: C, 69.60; H, 10.78; N, 12.49. Found: C, 69.71; H, 10.60; N, 12.41.

The slightly brown solution (for the infrared bands in the metal–carbonyl region see the Results section) was distilled at ordinary pressure. A fraction of 4.0 g. of N-cyclohexylformamide [b.p. 130–136° (8 mm.), lit.[14] 135–140° (10 mm.)] was then collected by distillation under reduced pressure.

Anal. Calcd. for $C_7H_{13}NO$: C, 66.10; H, 10.30; N, 11.01. Found: C, 66.25; H, 10.35; N, 10.93.

A residue of 10 g., being mainly decomposition products of the catalyst and dicyclohexylurea, was left after the distillation.

(b) **Carbonylation of *n*-Butylamine (Run 6 in Table I).**—Butylamine (57.9 g., 78.3 ml., 0.79 mole) was charged in the autoclave together with 170 ml. of heptane and 2.26 g. of $Mn_2(CO)_{10}$. Carbon monoxide (131 atm.) was compressed and the autoclave stirred and heated at 180–200° for about 12 hr. After cooling, no gas absorption could be observed. The gas was vented (hydrogen detected by gas chromatography) and the contents of the autoclave collected by washing with heptane. By titration with aqueous HCl 18 g. of unreacted amine was found to be contained in the solution. The latter was filtered and then cooled to about −50°. The colorless crystalline 1,3-di-*n*-butylurea so separated was filtered and dried *in vacuo* (31.9 g., 46.9% yield). The m.p. was 63–65° and mixed with an authentic sample of the urea (m.p. 71–72°, lit.[15] 67–68°, lit.[16] 70°), prepared from $COCl_2$ and *n*-butylamine, the m.p. was 65–68°. After crystallization from *n*-heptane, 90% of the original product melted at 69–71°. After distillation of excess amine and heptane, a liquid residue of 10.2 g. was left; this, on distillation under reduced pressure, gave 5.5 g. (6.8% based on the starting amine) of N-butylformamide [b.p. 121–124° (15 mm.), lit.[14] 122–123° (16 mm.)] and 4 g. of a brown solid residue, mainly decomposition products of the catalyst and the dialkylurea.

(c) **Carbonylation of Aniline (Run 11 in Table I).**—Aniline (120 g., 117.4 ml., 1.29 moles), heptane (134 ml.), and $Mn_2(CO)_{10}$ (2.26 g.) were treated for 48 hr. under 190 atm. of carbon monoxide pressure. After cooling, the gas was vented (traces of hydrogen). By concentration under reduced pressure at room

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temperature, the yellow-orange solution from the autoclave yielded 1.2 g. of an orange crystalline solid identified by infrared spectrum as pure $Mn_2(CO)_{10}$. By distillation at reduced pressure, unchanged aniline (104 g.) was recovered, and from a residue of 10 g., 1,3-diphenylurea (8 g., 5.8%), m.p. 229–230° (lit. 235°), was obtained after crystallization from ethyl alcohol.

Results

By heating primary aliphatic amines, such as cyclohexylamine and *n*-butylamine, to 180–200° with CO under pressure, in the presence of $Mn_2(CO)_{10}$ or $CH_3Mn(CO)_5$, the corresponding 1,3-dialkylureas were obtained in good yields, as shown in Table I. Small yields of N-alkylformamides were normally also obtained, but their formation is probably due to some reaction pathway unrelated to the main one, since the formamides were also found in the presence of anhydrous manganese(II) acetate or in the absence of any manganese compound at all (see runs no. 4 and 7, respectively, in Table I). Little or no gas absorption was observed during the reaction and hydrogen was detected in the gas phase by gas chromatography. On this basis, the over-all reaction leading to the disubstituted ureas can be written as

$$2H_2N\text{-}R + CO \longrightarrow CO(NHR)_2 + H_2 \qquad (3)$$

Secondary and tertiary aliphatic amines failed to react and aniline gave small yields of 1,3-diphenylurea over very long reaction times. In the latter case, about 50% of the $Mn_2(CO)_{10}$ employed could be recovered unchanged after 48 hr. at about 190°.

The failure to isolate any dialkylurea from run no. 4 carried out in the presence of anhydrous manganese(II) acetate indicates the obvious but nonetheless important conclusion that no carbonylation reaction of the amine can be obtained unless CO groups are present in the coordination sphere of the metal. No significant differences in the effectiveness of $Mn_2(CO)_{10}$ and $CH_3Mn(CO)_5$ to promote the carbonylation could be observed. Decacarbonyldimanganese is probably converted during the reaction into some ionic species of the type $[Mn(CO)_{6-n}L_n]^+[Mn(CO)_{5-n}L_n]^-$ (I), where L can be the amine or the corresponding alkylformamide or dialkylurea. The infrared spectrum of the solution from run no. 1 of Table I showed absorptions at 2178, 2122, 2089, 2073, 2009, 1976, 1957, 1939, 1871, 1854, and 1800 cm.$^{-1}$, to be compared with the bands of $Mn_2(CO)_{10}$ in the same conditions at 2047, 2014, and 1985 cm.$^{-1}$. From the rather complicated infrared spectrum it appears that at the end of reaction $Mn_2(CO)_{10}$ was completely converted into several compounds. However, assuming that all the above-mentioned bands are due to genuine CO stretching vibrations, two groups of them can be first taken into account, one from 2178 to 2073 cm.$^{-1}$ and the other from 1871 to 1800 cm.$^{-1}$. The latter group should be attributed to some substituted carbonylmanganate, $[Mn(CO)_{5-n}L_n]^-$. In fact, $[Mn(CO)_5]^-$ shows[17] two bands at 1898 and 1863 cm.$^{-1}$ and the shift to lower wave numbers is in good accordance with the presence in the anion of amine or alkylformamide groups. The former have been proposed[18] to be purely σ-bonded to the metal, whereas π-donor properties have been recently attributed[19] to the latter. The group of bands from 2178 to 2073 cm.$^{-1}$ can be attributed to some cationic species $[Mn(CO)_{6-n}L_n]^+$, a known example of this type being the ethylene cation[20] $[Mn(CO)_5C_2H_4]^+$, which absorbs at 2165, 2083, and 2062 cm.$^{-1}$. Finally, the intermediate group of bands at 2009, 1976, 1957, and 1939 cm.$^{-1}$ can be tentatively assigned to some uncharged species such as $[Mn(CO)_{5-n}L_n]_x$, $x = 1$ or 2.

The presence of ionic species of type I in the mixtures from the carbonylation reaction of amines is in accordance with the known chemistry of metal carbonyls which give rise to valence disproportionation in the presence of amines and Lewis bases (L) in general. The best known[21] example is $Co_2(CO)_8$ which gives $[CoL_6][Co(CO)_4]_2$ (II), but similar reactions have been described also in the case of $Mn_2(CO)_{10}$[22] and $V(CO)_6$.[23] There is evidence[21] that the first step to II is an unstable species of the type $[Co(CO)_4L][Co(CO)_4]$. Hieber and co-workers have confirmed this view with some infrared evidence that the species $[Mn(CO)_5L]^+[Mn(CO)_5]^-$ is formed in the room temperature reaction of $Mn_2(CO)_{10}$ with *n*-butylamine.

Discussion

From the present study it appears that $Mn_2(CO)_{10}$ and $CH_3Mn(CO)_5$ are unique among metal carbonyls in the following respects: (a) only primary amines give the carbonylation reaction to dialkylureas; (b) ammonia and secondary and tertiary amines react either very slowly or not at all; (c) aniline reacts very slowly; (d) dialkylureas are the chief products in each case and only small amounts of alkylformamides are formed. As far as points (a), (b), and (c) are concerned, there is no straightforward explanation of the experimental facts and probably both the basic strength of the amine and steric factors play an important role. The results of the investigation on the reaction mixtures seem to indicate, however, that an essential prerequisite for a successful carbonylation of the amine is the consumption of $Mn_2(CO)_{10}$ to the cation–anion species. The recovery of a large amount of unreacted $Mn_2(CO)_{10}$ from the reaction with aniline seems to support this view.

As for point (d), the poor yields of alkylformamides must be related to the fact that the over-all reaction (3) occurs in two steps

$$H_2N\text{-}R + CO \xrightarrow{k_1} HCONHR \qquad (3a)$$

$$HCONHR + H_2N\text{-}R \xrightarrow{k_2} CO(NHR)_2 + H_2 \qquad (3b)$$

with k_2 being probably much larger than k_1. If the opposite occurs, little or no dialkylurea can be formed.

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Since both steps take place in the coordination sphere of the metal, the condition for the formation of the dialkylurea is that the alkylformamide formed in the first step is retained on the metal and undergoes a fast nucleophilic attack on the formyl carbon atom by a second molecule of amine. The second step is perhaps the most difficult to interpret. In order to account for the dehydrogenating properties shown by the manganese system it is probably necessary to invoke the intermediate formation of a metal–hydrogen bond. It is hoped that further work which is presently in progress with different organic substrates will help us to understand this particular point.

One of the possible answers to the question of why manganese is capable of yielding almost exclusively dialkylureas, whereas other metal carbonyls show a lower tendency to do so, is that the higher coordination number of manganese and consequently the large number of π-acceptor CO groups bonded to it facilitates the binding of the formamide group in the coordination sphere. For the same kind of reasons, it is believed that the formation of the dialkylureas occurs on the cationic part of the previously mentioned ionic species $[Mn(CO)_{6-n}L_n]^+[Mn(CO)_{5-n}L_n]^-$, which is probably the active catalyst of the carbonylation reaction.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
PURDUE UNIVERSITY, LAFAYETTE, INDIANA

The Molecular Weights of Trimethylgallium and Triethylgallium in Solution

BY NORBERT MULLER AND ARTHUR L. OTERMAT

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Proton magnetic resonance spectroscopy, vapor pressure lowering measurements, and freezing point determinations have been used to show that both trimethylgallium and triethylgallium are monomeric in solutions in benzene or cyclopentane. Additional evidence is also presented to support the conclusion that trimethylindium is not associated in benzene. Earlier reports to the contrary notwithstanding, it now appears that aluminum is the only metal in group III whose saturated trialkyl derivatives are appreciably dimerized in the liquid state through formation of alkyl-bridge bonds.

Introduction

There have been many reports on the tendency of the trialkyl derivatives (R_3M) of the metals of group III to form alkyl-bridged, associated species in solution.[1] When work on these compounds was begun in this laboratory, the available information could be summarized as follows[1,2]: R_3B: monomeric for R = methyl or ethyl. R_3Al: dimeric for R = methyl; higher alkyl derivatives decreasingly associated as steric requirements of R increase. R_3Ga: methyl derivative evaporates with $\Delta H = 7.8$ kcal./mole to give monomeric vapor, but no molecular weight studies have been made on the compound in the liquid state; ethyl derivative also forms monomeric vapor, with $\Delta H = 10.2$ kcal./mole, but is about 70% dimeric in solution in benzene or cyclohexane. R_3In: methyl derivative tetrameric in benzene solution but sublimes with $\Delta H = 13.8$ kcal./mole giving monomeric vapor; ethyl derivative monomeric both in benzene and in vapor phase; propyl derivative monomeric in benzene. R_3Tl: monomeric in benzene solution for R = methyl or ethyl.

Because these findings seemed to fit into no self-consistent pattern we decided to reinvestigate several of these compounds using proton magnetic resonance and other methods to determine the nature of the dissolved species and, if possible, the heats and free energies of association. Our first conclusion,[3] that trimethylindium dissolves as a monomer rather than a tetramer, is further supported by new evidence reported below. In addition we now find that both trimethylgallium and triethylgallium are actually monomeric in solution. It thus appears that aluminum is the only metal of group III whose saturated alkyl derivatives are associated in solution and that the behavior of the trialkyls of the other group III metals is quite regular.

Experimental

Trimethylindium was prepared from indium and dimethylmercury as already reported.[3]

Trimethylgallium was made from gallium tribromide and trimethylaluminum.[4] The details of the preparation have been described elsewhere.[5] After fractionation on the vacuum line, a product with 8.5 mm. vapor pressure at −28° was obtained; the corresponding value from the literature[6] is 8.41 mm. The purity was checked using the n.m.r. spectrum of a 5 mole % solution of the product in cyclopentane, which showed only a single methyl peak 1.48 p.p.m. upfield from the solvent signal. Taken by itself, this does not prove that the product was free from trimethylaluminum, since the methyl signals from the two compounds would probably coalesce as a result of alkyl group ex-

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