Carbon Monoxide Insertion Reactions. I. The Carbonylation of Methyl Manganese Pentacarbonyl and Decarbonylation of Acetyl Manganese Pentacarbonyl

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The equilibrium and the rates of the forward and reverse reactions in the system $CH_3Mn(CO)_5 + CO = CH_3CO-Mn(CO)_5$ have been studied at atmospheric pressure of carbon monoxide in various solvents and at several temperatures. The reaction is first order in both $CH_3Mn(CO)_5$ and CO. In $(CH_3CH_2OCH_2CH_2)_2O$, the solvent most used, the following data have been obtained: For the equilibrium at 30°, $K = 367$ l. mole^{-1}, $\Delta H^0 = -12.6$ kcal. mole^{-1}, $\Delta F^0 = -3.55$ kcal. mole^{-1}, $\Delta S^0 = -30.0$ cal. mole^{-1} deg.$^{-1}$. For the forward reaction at 30°, $k_1 = 8.99 \times 10^{-3}$ l. mole^{-1} sec.$^{-1}$, $\Delta H^* = 14.2$ kcal. mole^{-1}, $\Delta F^* = 20.6$ kcal. mole^{-1}, $\Delta S^* = -21.1$ cal. mole^{-1} deg.$^{-1}$. For the reverse reaction at 30°, $k_2 = 2.46 \times 10^{-5}$ sec.$^{-1}$, $\Delta H^* \approx 27$ kcal. mole^{-1}, $\Delta F^* \approx 24$ kcal. mole^{-1}, $\Delta S^* \approx 10.5$ cal. mole^{-1} deg.$^{-1}$. The effect of changing the solvent appears to be mainly a function of the bulk dielectric constant in stabilizing a somewhat polar transition state and specific, molecular solvent participation does not appear to be important in the solvents used. Possible mechanisms are discussed and one involving direct combination of $CH_3Mn(CO)_5$ with CO is shown to fit all the known facts and is preferred although a mechanism involving the rapid pre-equilibrium $CH_3Mn(CO)_5 = CH_3COMn(CO)_4$ cannot be ruled out at this stage.

Introduction

Carbon monoxide insertion reactions are those in which a metal-alkyl or metal-aryl group, M–R, is converted by treatment of the compound with carbon monoxide to a metal-acyl group, MCOR. The first such reaction to have been directly observed occurs with methylmanganese pentacarbonyl.[2] The same workers later showed[3] that the thermal decomposition of acetylmanganese pentacarbonyl labelled with ^{14}C in the acetyl carbonyl group did not give appreciable amounts of activity in the gas phase, while acetylmanganese pentacarbonyl formed from methylmanganese pentacarbonyl and ^{14}CO under pressure did not have activity in the acetyl group. These experiments thus show that gaseous carbon monoxide does not directly enter nor directly leave the acetyl position but rather goes in and out by way of the $-Mn(CO)_5$ part of these molecules in the system

$$CH_3Mn(CO)_5 + CO = CH_3COMn(CO)_5$$
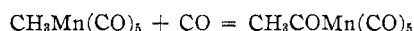
It also has been shown that benzoylmanganese pentacarbonyl loses carbon monoxide to form phenylmanganese pentacarbonyl.[4]

It also is known that methylmanganese pentacarbonyl and phenylmanganese pentacarbonyl react with aliphatic and aromatic amines, and also ammonia, to yield the corresponding RCOMn(CO)$_4$ amine compounds[5] and the investigators of these reactions gave reasons for believing that they, like the carbonylation reaction, proceed by a concerted mechanism with a transition state of the sort represented by I. More recently Booth and
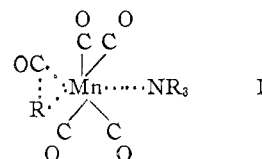
Chatt[6] have discovered that alkyl and aryl derivatives of Pd(II), Pt(II), Ni(II), and Co(II) undergo reactions typified by

trans-[Pt((C₂H₅)₃P)₂BrCH₃] + CO =
trans-[Pt((C₂H₅)₃P)₂Br(OCCH₃)]
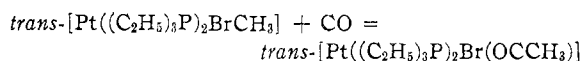
Like the reaction with the methylmanganese pentacarbonyl, these are reported to be reversible.

Aside from the tracer study already mentioned and inferences drawn from studies of the oxo reaction, there has been no information on the kinetics and mechanisms of carbon monoxide insertion reactions. Because the manganese pentacarbonyl species are fairly convenient for study and may well

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

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

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

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

(6) G. Booth and J. Chatt, *Proc. Chem. Soc.*, 67 (1961).

be mechanistically analogous to the reactions in the cobalt carbonyl system, a thorough study of the equilibrium and kinetic behavior of the $CH_3Mn(CO)_5$-$CH_3COMn(CO)_5$ system has been carried out and is reported here. We hope in a future paper to report the results of similar studies of other systems so that the dependence of reaction rate and equilibrium constants on the nature of the group R in $RMn(CO)_5$ and $RCOMn(CO)_5$ can be used to obtain further information about the reaction mechanism.

Results

The specific rate constants and the equilibrium constant for the system studied are defined by

$$CH_3Mn(CO)_5 + CO \underset{k_2}{\overset{k_1}{\rightleftharpoons}} CH_3COMn(CO)_5 \quad (1)$$
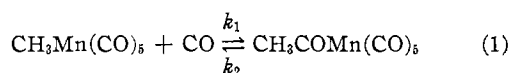
$$K = \frac{[CH_3COMn(CO)_5]}{[CH_3Mn(CO)_5][CO]} = \frac{k_1}{k_2} \quad (2)$$

The brackets are used to indicate concentrations in moles per liter.

The rates of the carbonylation reaction were measured in such a way that the pressure of CO, and hence its concentration in solution, remained constant throughout a particular run, and, as shown below, the forward reaction is first order in both CO and $CH_3Mn(CO)_5$. For such a reversible system, the equation for k_1 can be derived straightforwardly. In equation 3 t represents time

$$k_1 = \frac{1}{t} \frac{[CH_3COMn(CO)_5]_{eq}}{[CO][CH_3Mn(CO)_5]_0} \times$$

$$\ln \frac{[CH_3COMn(CO)_5]_{eq}}{[CH_3COMn(CO)_5]_{eq} - [CH_3COMn(CO)_5]_t} \quad (3)$$

in seconds, and the subscripts to the brackets signify that the concentrations are those at equilibrium, initially, and at time t, for subscripts eq, 0, and t, respectively.

Reaction Order.—The carbonylation reaction was shown to be first order in $CH_3Mn(CO)_5$ by measurements of the rate of uptake of CO at 30° in six different solvents, the pressure of CO over the reaction mixture being maintained constant at *ca.* one atmosphere by the manostatic device described in the experimental section. The results obtained were fitted to equation 3 to obtain values of the rate constants, k_1, in the various solvents. The concentrations of CO were obtained in separate measurements of the solubility of CO in the various solvents. In every case the experimental points defined the line required by equation 3 to well within the expected experimental errors (Figure 1).
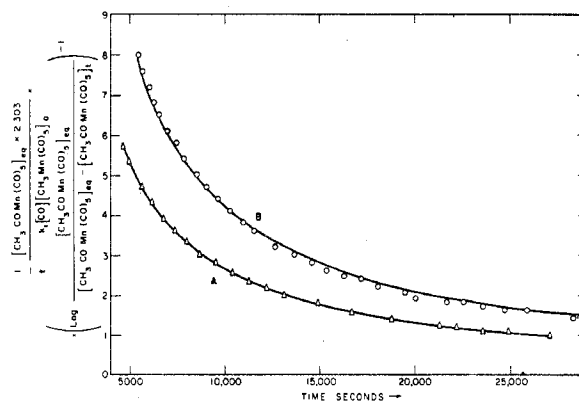

Fig. 1.—Experimental points and calculated curves for the carbonylation of $CH_3Mn(CO)_5$ in $(CH_3CH_2OCH_2CH_2)_2O$ at 30° at two pressures of carbon monoxide: A, CO pressure, 752 mm.; B, partial pressure of CO, 361 mm. Both curves are calculated using the same rate constant, k_1, viz., 8.99×10^{-3} l. $mole^{-1} sec.^{-1}$.

In order to determine the order of the carbonylation reaction in carbon monoxide two runs were made at 30° in β,β'-diethoxydiethyl ether, one using pure CO at a pressure of 751.5 mm. and the other using a mixture of CO with nitrogen such that the partial pressure of CO was 361 mm., *i.e.*, about half of its magnitude in the first run. Both sets of results when inserted in equation 3 gave the same rate constant k_1. Thus the validity of the rate expression

$$-\frac{d[CH_3Mn(CO)_5]}{dt} = \frac{d[CH_3COMn(CO)_5]}{dt} =$$

$$k_1[CO][CH_3Mn(CO)_5] \quad (4)$$

is established. The experimental points and theoretical curves for these two runs are shown in Figure 1 and may be taken as representative of the density of points and extent of agreement with calculated curves in all of the runs.

Temperature Dependence of the Equilibrium Constant.—From the data recorded in Table I it follows by straightforward thermodynamic computations that reaction 1 in β,β'-diethoxydiethyl

TABLE I

TEMPERATURE DEPENDENCE OF THE SPECIFIC RATE CONSTANT, k_1, AND THE EQUILIBRIUM CONSTANT, K, FOR THE CARBONYLATION OF METHYLMANGANESE PENTACARBONYL IN $(CH_3CH_2OCH_2CH_2)_2O$

T, °C.	k_1 (l. $mole^{-1} sec.^{-1}$)	K (l. $mole^{-1}$)
20	3.89×10^{-3}	755
30	8.99×10^{-3}	367
40	19.7×10^{-3}	190
49.6		100

ether at 30° is characterized by the following thermodynamic changes

$$\Delta H^0 = -12.65 \pm 0.1 \text{ kcal. mole}^{-1}$$
$$\Delta F^0 = -3.55 \pm 0.1 \text{ kcal. mole}^{-1}$$
$$\Delta S^0 = -30.0 \pm 0.6 \text{ cal. mole}^{-1} \text{ deg.}^{-1}$$

Owing to lack of information the activity coefficients were assumed to be unity.

Temperature Dependence of Reaction Rates.—The variation of the rate of the carbonylation reaction with temperature was studied using the solvent β,β'-diethoxydiethyl ether. The results are collected in Table I. A plot of the logarithms of the rate constants, k_1, vs. the reciprocal of absolute temperature yields a straight line from which the Arrhenius activation energy, E_a, is found to be 14.8 kcal. mole^{-1}. From this and the specific rate constant at 30°, the thermodynamic parameters of the activated state at 30° were calculated.[7]

$$\Delta H_1^* = 14.2 \text{ kcal. mole}^{-1}$$
$$\Delta F_1^* = 20.6 \text{ kcal. mole}^{-1}$$
$$\Delta S_1^* = -21.1 \text{ cal. mole}^{-1} \text{ deg.}^{-1}$$

The approximate experimental activation energy for the decarbonylation of acetylmanganese pentacarbonyl was determined in β,β'-diethoxydiethyl ether by direct measurements of the rate constant k_2 at two temperatures, 30 and 40°. For this reaction the rate constant is given by the equation

$$k_2 = \frac{1}{t}\frac{[CH_3Mn(CO)_5]_{eq}}{[CH_3COMn(CO)_5]_0} \times$$
$$\ln \frac{[CH_3Mn(CO)_5]_{eq}}{[CH_3Mn(CO)_5]_{eq}[CH_3Mn(CO)_5]_t}$$

in which the symbols have the same meaning as in equation 3. At both temperatures the experimental points (obtained by measuring the volume of CO evolved as a function of time) gave an excellent fit to equation 4 with k_2 values of 2.85×10^{-5} sec.$^{-1}$ and 12.6×10^{-5} sec.$^{-1}$ at 30 and 40°, respectively. From these E_a was found to be 28.2 kcal. mole^{-1}. The following thermodynamic parameters of formation of the activated complex for the reverse reaction calculated from the directly measured E_a and k_2 at 30° are in satisfactory agreement with those which can be calculated from the parameters for the forward reaction and for the equilibrium, the latter being given in parentheses for comparison

(7) S. Glasstone, K. J. Laidler, and H. Eyring, "The Theory of Rate Processes," McGraw-Hill, New York, N. Y., 1941, pp. 195–199.

$$\Delta H_2^* = 27.6 \ (26.9) \text{ kcal. mole}^{-1}$$
$$\Delta F_2^* = 24.1 \ (24.2) \text{ kcal. mole}^{-1}$$
$$\Delta S_2^* = 11.7 \ (8.9) \text{ cal. mole}^{-1} \text{ deg.}^{-1}$$

This agreement shows that there is no serious error in any of the measurements since the rate measurements are entirely independent of one another.

Solvent Effects.—In order to clarify further the mechanism of carbonylation of methylmanganese pentacarbonyl, and particularly to determine the role of the solvent, measurements have been made in a number of solvents chosen to cover a considerable range in both dielectric constant and nucleophilicity. The main results of these studies are presented in Table II and in Figure 2. As Figure 2 shows, there is a fairly good correlation between log k_1 and the appropriate function of the dielectric constant of the solvent, $(D-1)/(2D+1)$. A straight line relationship of this kind is expected when the solvent does not become involved in the transition state on a molecular basis but merely influences the energy of the more or less polar transition state by virtue of its bulk dielectric constant.[8]

Discussion

We believe that all of the results reported here support the belief that the activated complex has a structure such as is indicated by II and
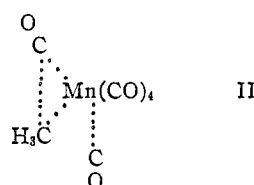
that this forms by direct combination of CO with $CH_3Mn(CO)_5$ without specific participation by solvent molecules in the solvents we have used. We wish to point out that while the transition state (I) suggested by Keblys and Filbey[5] for the amine reaction was drawn by them to show attack by the base in a position such that it would become *trans* to the acetyl group in the product molecule, Keblys and Filbey did not offer any evidence regarding this detail of the stereochemistry of the transition state or the reaction products and we assume that the specificity indicated was not deliberate or intended to be taken literally. At the present time we are not prepared to offer any evidence concerning this detail of the mechanism of the carbonylation reaction itself and the above drawing (II) of the transition state

(8) Ref. 7, pp. 419–428.

TABLE II

SOLVENT EFFECTS ON RATE AND EQUILIBRIUM CONSTANTS AND THERMODYNAMIC CHANGES AT 30°

Solvent	Dielectric constant, D	$\dfrac{D-1}{2D+1}$	K	k_1	$k_2 = k_1/K$	$-\Delta H^0$, kcal. mole^{-1}	$-\Delta F^0$, kcal. mole^{-1}	$-\Delta S$, cal. mole^{-1} deg.$^{-1}$
β,β'-Diethoxydiethyl ether	5.68^a (25°)	0.379	367	8.99×10^{-3}	2.46×10^{-5}	12.6^b	3.55	30.0
β,β'-Dichlorodiethyl ether	21.2^b (20°)	.465	1800	2.02×10^{-2}	1.12×10^{-5}	12.2	4.52	25.3
n-Octyl chloride	4.96^b (30°)	.363	211	1.85×10^{-3}	8.74×10^{-6}	11.5	3.22	27.3
Di-n-butyl ether	3.06^b (25°)	.289	127	1.19×10^{-3}	9.38×10^{-6}	...	2.92	...
Mesitylene	2.27^b (20°)	.229	226	4.49×10^{-4}	1.99×10^{-6}	...	3.26	...
Dimethylformamide	26.6^c (25°)	.472	3314	2.19×10^{-2}	6.61×10^{-6}	18.1	4.88	43.6

^{a} Kindly measured for us by Mr. William Westphal of the Laboratory for Insulation Research, M.I.T. ^{b} Table of Dielectric Constants of pure liquids, National Bureau of Standards Circular 514, August 10, 1951. ^{c} Technical Bulletin on Dimethylformamide, E. I. du Pont de Nemours and Co., Inc.
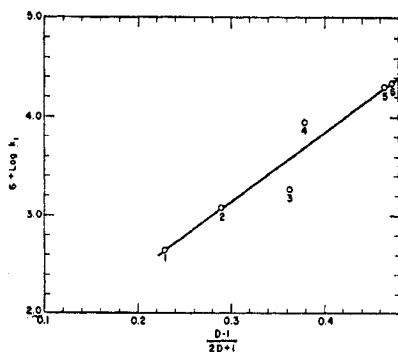

Fig. 2.—Plot showing the dependence of the rate constant, k_1, on dielectric constant of the solvent, at 30°, for the six solvents used: 1, mesitylene; 2, di-n-butyl ether; 3, n-octyl chloride; 4, β,β'-diethoxydiethyl ether; 5, β,β'-dichlorodiethyl ether; 6, dimethylformamide.

is not intended to convey any specification of stereochemistry.

The consistency of our results with this sort of mechanism may be summarized briefly as follows: The order of the carbonylation reaction as given in equation 4 is consistent with its having a molecularity of two as postulated. The fact that the entropy of activation (-21 cal. mole^{-1} deg.$^{-1}$) is a substantial fraction of the total ΔS of reaction (-30.0 cal. mole^{-1} deg.$^{-1}$) is consistent with the postulated transition state in which the CO has lost its translational entropy but several bonds in the activated complex are loose so that there still is appreciable vibrational entropy to be lost in the ultimate transformation to the final product. The solvent dependence of the rate constant is quite in accord with the assumption that the CO and $CH_3Mn(CO)_5$ combine directly to produce a polar activated complex without any specific, *i.e.* molecular, intervention by the solvent. More exactly, the basicity of the solvent does not

seem to be a governing factor in its influence on the reaction rate since there is no correlation between the rates and the expected relative nucleophilicities of the various kinds of solvent molecules, while the theoretically expected correlation between rates and solvent dielectric constants is fairly well obeyed. The deviations of the points for n-octyl chloride and β,β'-diethoxydiethyl ether perhaps suggest that when the dielectric constants are nearly the same while the basicity difference is extreme some specific dependence on solvent basicity may be manifest, perhaps because of the possibility of a relatively unimportant reaction path which does require specific participation of a nucleophilic solvent molecule.[9] The increase in rate constant with increasing dielectric constant means that the activated complex is more polar than the reactants. This is quite plausible in view of the reported[10] dipole moments of $CH_3Mn(CO)_5$ (0.80) and $CH_3COMn(CO)_5$ (2.27).

Finally, we must consider the consequences of the fact that while our rate expression (4) is perfectly consistent with the mechanism we propose, it also is consistent with a mechanism in which CO reacts not with $CH_3Mn(CO)_5$ to give

(9) In this connection it can be mentioned that solutions of $CH_3Mn(CO)_5$ in tetrahydrofuran and in β,β'-diethoxydiethyl ether, *i.e.*, the more strongly basic solvents, are yellow-orange and show an infrared band at 1650 cm.$^{-1}$. The intensity of this band increases with time, reaching a constant value only after several hours. A reasonable explanation of these observations is that in a good nucleophilic solvent an equilibrium of the type [$CH_3Mn(CO)_5$] = [$CH_3COMn(CO)_4$(solvent)] is set up. In timed experiments in β,β'-diethoxydiethyl ether we have shown that the time required to attain this equilibrium is greater than that required to reach the equilibrium position in the carbonylation reaction, thus ruling out the solvent complex as a significant intermediate in the carbonylation reaction.

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

the activated complex but with some species in labile equilibrium with $CH_3Mn(CO)_5$. Such a species might be $CH_3COMn(CO)_4$. In their proposals regarding the mechanism of the oxo reaction and, more specifically, of the carbonylation of alkylcobalt tetracarbonyl molecules, Breslow and Heck[11] have contended that a labile equilibrium of the type

$$RCo(CO)_4 = RCOCo(CO)_3$$
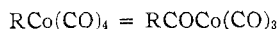
exists and that an incoming nucleophile or base reacts directly with the acylcobalt tricarbonyl rather than with the coördinately saturated alkylcobalt tetracarbonyl. Obviously, a parallel situation

$$CH_3Mn(CO)_5 = CH_3COMn(CO)_4 \qquad (5)$$
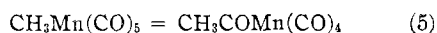
could be considered in the present case. We believe that our solvent effect studies provide some evidence against this since more basic solvents would be expected to combine with $CH_3COMn(CO)_4$ and hence decrease the rate of reaction. It also may be noted that the main evidence offered by Breslow and Heck for the presence of $RCOCo(CO)_3$ species in the cobalt system is the occurrence of an infrared band at 5.8 microns ($\sim$1725 cm.$^{-1}$) in the infrared spectra of supposedly pure $RCo(CO)_4$ compounds in solution. However, these compounds are extremely unstable and recently[12] it has been shown that one of the decomposition products of $CH_3Co(CO)_4$ is acetone, which has a band at about this position. Thus, while the data presented here do not allow us to rule out the possibility that a rapid pre-equilibrium such as (5) precedes reaction, we find no evidence to suggest that such a mechansim is preferable to the simpler one discussed earlier.

Experimental

Materials.—Methylmanganese pentacarbonyl was prepared by the method of Closson, *et al.*,[2] from $NaMn(CO)_5$ and dimethyl sulfate. Yields as high as 75% were obtained

by operating at about $-40°$ with a 50% excess over the calculated amount of the methylating agent and by using diethyl ether as a solvent. The reaction appeared to be complete after a few minutes and the solvent then was removed at 50 mm. and methylmanganese pentacarbonyl sublimed at 40–60°(15 mm.) from the solid residue. The compound was purified by crystallization from *n*-pentane and its purity checked by elemental analyses and by its infrared spectrum.

Acetylmanganese pentacarbonyl was prepared by a slight modificatio nof the method of Closson, *et al.*,[2] from $NaMn(CO)_5$ and CH_3COCl (50% excess) at about $-40°$ using diethyl ether as solvent. In order to obtain a product of high purity the entire preparation was carried out under an atmosphere of carbon monoxide. When the reaction appeared to be complete (a few minutes after addition of CH_3COCl to the sodium salt), *n*-pentane was added to the reaction mixture, the solution filtered to remove NaCl and the filtrate cooled to about $-70°$. The white crystalline compound, sealed in a capillary under carbon monoxide, melted at 56–57° with gas evolution. It was used for the kinetic experiments without further purification.

Mesitylene, reagent grade from Eastman Kodak Company, was refluxed over sodium and fractionated. Di-*n*-butyl ether and β,β'-diethoxydiethyl ether were distilled from lithium tetrahydridoaluminate in a nitrogen atmosphere and stored for short periods under nitrogen. *n*-Octyl chloride, β,β'-dichlorodiethyl ether, and dimethylformamide were fractionated under reduced pressure. Carbon monoxide was obtained from the Matheson Company in a stainless steel tank and used without further purification.

Apparatus and Procedures for the Measurements.—The kinetics and equilibrium were studied by measuring the volume of carbon monoxide absorbed or evolved in systems containing weighed quantitites of $CH_3Mn(CO)_5$ or $CH_3COMn(CO)_5$ and known volumes of solvent. The gas volumetric apparatus was substantially similar to that described by Ercoli, Chini, and Massi Mauri[13] and shown in Figure 3. It consists of a 100-ml. buret, graduated to 0.2
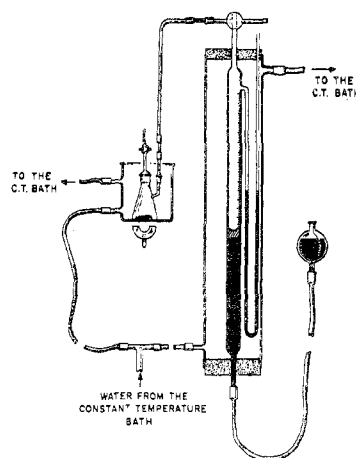
Fig. 3.—A sketch of the manostatic apparatus used to follow the uptake or evolution of carbon monoxide.

(11) D. S. Breslow and R. F. Heck, *Chem. & Ind.* (London), 467 (1960); R. F. Heck and D. S. Breslow, *J. Am. Chem. Soc.*, **82**, 4438 (1960); R. F. Heck and D. S. Breslow, Abstracts of Papers, 139th National Meeting of the American Chemical Society, St. Louis, March, 1961, p. 39-R.

(12) W. Hieber, W. Beck, and E. Lindner, *Z. Naturforsch.*, **16b**, 229 (1961).

(13) R. Ercoli, P. Chini, and M. Massi Mauri, *Chim. e Ind.* (Milan), **41**, 132 (1959).

ml., connected through a 3-way stopcock and capillary tubing (1.5 mm. i.d.) to a 50-ml. two-neck Erlenmeyer flask containing a glass-covered, magnetically activated stirring bar. The reaction flask and buret both were surrounded by jackets through which water from a constant temperature bath was rapidly circulated. The temperatures within these jackets remained constant to ±0.05° during a run. The leveling liquid in the buret was mercury but the actual meniscus consisted of a few ml. of the same solvent used in the reaction flask. In order to insure prompt and accurate leveling the top of the buret was connected to the atmosphere through a U tube of 3 mm. i.d. half filled with the solvent.

In a typical kinetic run, 30.0 ml. of solvent was introduced into the reaction flask and carefully saturated with carbon monoxide at room temperature by repeated evacuations to ~12 mm., followed by restoration of one atmosphere of fresh carbon monoxide. The buret then was closed off from the reaction flask and with a positive pressure maintained the flask was opened quickly and the sample of the manganese compound inserted. As this was done the valve controlling the flow of carbon monoxide was opened simultaneously and then closed so that an outflowing stream of carbon monoxide brisk enough to prevent entry of air was maintained during the few seconds required to insert the sample. The samples were about 0.4 g. of $CH_3Mn(CO)_5$ or $CH_3COMn(CO)_5$ sealed in thin-walled vials, 0.5–1.0 ml. in capacity. The entire apparatus then was thermostated for several hours, usually overnight, to permit attainment of equilibrium conditions. The buret then was read and the vial crushed to begin the run.

Particular care was taken to provide effective stirring so that diffusion would not be rate controlling. By means of separate experiments the approximate minimum stirring rate required was found and in all runs the stirring was made far more vigorous. The excellent reproducibility of the results is in itself good evidence that the stirring was adequate to eliminate diffusion control.

Buret readings were corrected for temperature, atmospheric pressure as read frequently during a run from a nearby barometer, and the vapor pressure of the solvent,[14] and the volume of carbon monoxide which had been absorbed or evolved at a given time was converted to moles from which the concentrations of $CH_3Mn(CO)_5$ and $CH_3COMn(CO)_5$ present at that time were calculated. The equilibrium concentrations required for insertion in equations 2, 3, and 4 were calculated after allowing the system to react until no further change in the quantity of carbon monoxide was detectable. The values of k_1 recorded in Tables I and II were those required to give a curve which, by trial and error, was found to fit the data best between 5 and 80% of conversion at equilibrium. The mean deviation of points from a given curve was about ±4%.

Measurement of Carbon Monoxide Solubilities.—It was necessary to measure the solubility of carbon monoxide in the various solvents used and at the various temperatures. This was done using the gas volumetric apparatus in the

following way: The buret containing carbon monoxide and the flask containing 30.0 ml. of solvent were thermostated several hours. Using the 3-way stopcock the solvent then was connected to vacuum for about 10 min. while being stirred vigorously. A trap at −70° was placed between the bulb and the vacuum line to trap solvent vapors; this condensate later was weighed and an appropriate correction made to obtain the volume of solvent remaining in the bulb. The stopcock then was turned so as to disconnect the flask from the vacuum line and connect it with the buret. After equilibrium had been reached the buret was read. Knowing the free volume (the volume which could be evacuated minus the volume of the solvent present), the barometric pressure, the equilibrium vapor pressure of the solvent at the temperature of the measurement, and the temperature, the solubility was calculated. In Table III the results are given, expressed as the Bunsen

TABLE III

SOLUBILITY OF CO IN DIFFERENT SOLVENTS AT VARIOUS TEMPERATURES

Solvent	Temperature, °C.	Bunsen coefficient, α^a
β,β'-Diethoxydiethyl ether	10	0.1535
	20	.1550
	30	.1565
	40	.1580
β,β'-Dichlorodiethyl ether	20	.0588
	30	.0686
	40	.0785
n-Octyl chloride	25	.1840
	(30	.1876)^b
	40	.1952
Di-n-butyl ether	30	.2077
Mesitylene	30	.1416
Dimethylformamide	30	.0818
	40	.0908

^{a} Defined as ml. of CO at 1 atm. and 0° dissolved by 1 ml. of solvent when the partial pressure of CO is 1 atm. ^{b} Interpolated.

coefficients. These data show an increase of solubility with temperature, a relatively rare situation for a gas and one which connotes a negative heat of solution. Similar results for carbon monoxide in other liquids already have been reported.[16]

Determination of Reaction Order in Carbon Monoxide. —Because the gas volumetric apparatus could not be successfully operated at total internal pressures differing significantly from barometric pressure it was necessary to devise a method of lowering the partial pressure of carbon monoxide while maintaining the total gas pressure with an inert diluent gas. For this purpose, a mixture of nitrogen and carbon monoxide containing 47.9% CO by volume

(14) Care was taken to use solvents with relatively low vapor pressures at room temperature. Vapor pressure data were obtained from the literature or, when not found, were deduced from Dreisbach's tables.[15]

(15) R. R. Dreisbach, "Pressure-Volume-Temperature Relationships of Organic Compounds," Handbook Publishers, Inc., New York, N. Y., 1952.

(16) A. Seidell and W. F. Linke, "Solubilities of Inorganic and Metal-Organic Compounds," Vol. I, 4th ed., D. Van Nostrand Co., Inc., New York, N. Y., 1958. In this compilation the solubilities are given as Ostwald coefficients which show a very marked increase with temperature. The Bunsen coefficients obtained from them by suitable corrections in most cases continue to show definite though smaller increases.

(determined by absorption analysis in a Cu(I) solution)[17] was used to saturate the solvent, β,β'-diethoxydiethyl ether, and fill the reaction bulb at 30°. A kinetic run then was carried out in the normal manner except that the buret was filled with pure carbon monoxide and was closed off.

(17) W. W. Scott, "Standard Methods of Chemical Analysis," 5th ed., D. Van Nostrand Co., Inc., New York, N. Y., pp. 2349-50.

By manual operation of the stopcock this carbon monoxide was bled into the reaction bulb frequently so as to replace the carbon monoxide absorbed by the $CH_3Mn(CO)_5$. The composition of the gas and its total pressure in the reaction bulb thus were maintained essentially constant and the consumption of carbon monoxide as a function of time was followed.

Heat Capacities and Thermodynamic Functions of Iron Disulfide (Pyrite), Iron Diselenide, and Nickel Diselenide from 5 to 350°K. The Estimation of Standard Entropies of Transition Metal Chalcogenides[1]

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The heat capacities at low temperatures of purified, natural pyrite and synthetic samples of $FeSe_2$ and $NiSe_2$ were determined by the adiabatic technique. The data on pyrite are in good accord over the common range of measurement with those of Anderson, but not with those of Eucken and Schwers. The values of entropy and the free energy function, $-(F^0 - H_0^0)/T$ at 298.15°K. in cal. g.f.w.$^{-1}$ °K.$^{-1}$ are, respectively: 12.65 and 4.926 for FeS_2; 20.75 and 9.74 for $FeSe_2$; 24.74 and 12.36 for $NiSe_2$. The estimation of the entropies of transition element chalcogenides is discussed.

Introduction

This paper is an integral part of a continuing investigation concerned with the thermophysical properties and phase stabilities of transition element chalcogenides. It deals with three transition element dichalcogenides of which two, iron disulfide and nickel diselenide, possess the pyrite-type structure, and iron diselenide the marcasite-type structure. No heat capacity data are known for iron diselenide or for nickel diselenide, but in two papers[2,3] measurements on pyrite are reported which are in poor agreement with each other over the common range of measurement, and with a third in which enthalpy-type measurements are presented.[4] Another incentive for the redetermination of the heat capacity of pyrite was the marked divergence of pyrite from other substances in the Lindemann[5] relationship as presented by Zemansky[6] in the form $\theta = CT_m^{1/2} \times$

$M^{-1/2}V^{-1/3}$ in which θ is the Debye temperature, C a constant ~ 200, T_m the melting temperature, M the molecular weight and V the corresponding volume. The further striking departures of the entropies of substances with pyrite-type structure from those of other chalcogenides merit further study.

Experimental

Preparation of the Samples.—Iron disulfide was a pyrite from Bosmo grube, Nordland, Norway. It was crushed to a 30-80 mesh powder and then carefully separated from the accompanying minerals—mostly feldspar—by specific gravity and magnetic methods. Chemical analyses for iron and sulfur by gravimetric methods indicated 46.53 ± 0.03% by weight of iron and 53.45 ± 0.04% of sulfur (theoretical: 46.55% Fe, 53.45% S). Spectrochemical analysis indicated the presence of only the following contaminants (in p.p.m.): Mn (80), Ni (75), and Si (80). X-Ray powder photographs of the sample showed only the presence of lines from pyrite. Its lattice constant is $a = 5.416$ Å., in close agreement with the value $a = 5.4176$ Å. determined by Lepp.[7]

Iron diselenide was prepared from high-purity iron and selenium. Merck "Ferrum reductum pro analysi" was reduced with dry purified hydrogen gas at 900° until constant weight was attained. The spectrographic analysis showed as impurities (in p.p.m.): Mn ($\sim$10), Ni ($\sim$100),

(1) This work was supported in part by the Division of Research of the United States Atomic Energy Commission, Contract AT(11-1)-70, Project No. 5.

(2) A. Eucken and F. Schwers, *Ber. deut. physik. Ges.*, **14**, 578 (1913).

(3) C. T. Anderson, *J. Am. Chem. Soc.*, **59**, 486 (1937).

(4) R. Ewald, *Ann. Physik*, **44**, 1213 (1914).

(5) A. F. Lindemann, *Physik. Z.*, **11**, 609 (1910).

(6) M. W. Zemansky, "Heat and Thermodynamics," McGraw-Hill Book Co., New York, N. Y., 1957, p. 268.

(7) H. Lepp, *Am. Mineralogist*, **41**, 347 (1956).