TABLE I

QUANTITATIVE DATA FOR Ge_2H_6 DISPROPORTIONATIONS (ALL QUANTITIES IN MMOLES)

							Calcd values of *x*	
Temp, °C	Time, hr	*A* Ge_2H_6 in	*B* Ge_2H_6 out	*C* GeH_4 formed	*D* H_2 from GeH_x pyrolysis	*E* Ge in GeH_x	$2D/E$	$2D/[2(A-B)-C]$
−63	96	0.668	0.273	0.481	0.253	0.264	1.92	1.64[a]
−63	96	0.553	0.323	0.260	0.149	0.180	1.66	1.49[a]
−63	25	0.383	0.308	0.064	0.077	0.077	2.00	1.79[a]
−63	25	0.536	0.479	0.0696	0.0695	0.069	2.01	3.16[a]
−45	37	0.200	0	0.220	0.169	...	...	1.88
23[b]	24	0.188	0	0.244	0.0746	...	...	1.13
23	20	0.244	0	0.334	0.0676	...	...	0.88
23[c]	14	0.218	0	0.291	0.0789	...	...	1.09
23	13	0.247	0	0.321	0.0800	...	...	0.92
23	0.25	0.152	0.114	0.0417	0.0316	...	...	1.86[a]

[a] These values are relatively inaccurate because they require the difficult determination of the unreacted Ge_2H_6 (*B*). [b] Ammonia solution 1 *M* in NH_4NO_3. [c] $NH_3:Ge_2H_6 = 1:1$.

fact that the hydrogen in the germane produced and that formed in the pyrolysis of the GeH_x account for the hydrogen in the consumed digermane with an average discrepancy of ±1.2%. In the four experiments where a germanium balance could be calculated, the average discrepancy was ±3.5%.

In the −63° experiments, the solution was initially colorless, but, on standing, the solution turned yellow and a yellow precipitate formed. In the −45° experiment, a yellow precipitate formed quickly. In the room-temperature experiments, a blood red precipitate formed immediately.

Discussion

The results indicate that, in liquid ammonia solution, digermane disproportionates as: $Ge_2H_6 \rightarrow GeH_4 + GeH_2$. At temperatures above −63° (and even at that temperature on standing), the GeH_2 decomposes to germane and a yellow or red precipitate of GeH_x ($x < 2$). The higher the temperature, the more rapidly the GeH_2 decomposes, the lower the value of x, and the darker the color of the precipitated GeH_x. Although Glarum and Kraus[2] reported similar properties for GeH_2 prepared from bromobenzene and sodium germyl, their substance was more stable inasmuch as its solution in ammonia did not become colored on standing for 24 hr, and it could be isolated for a short time as a white solid at −33°.

In the hope that the solution at −63° contained a soluble GeH_2 species, the proton magnetic resonance spectrum of a 0.5 *M* Ge_2H_6 solution was obtained. The spectrum showed peaks corresponding to germane, digermane, and a series of three smaller peaks from 8 to 25 cycles upfield from germane, perhaps corresponding to a lower hydride. As the solution decomposed, the digermane peak decreased in amplitude, the germane peak increased, and the little peaks began to merge and broaden. By the time the digermane peak had disappeared, the little peaks were gone. Attempts to get better resolution by increasing the digermane concentration were unsuccessful, probably because of limited solubility of the lower hydride.

Efforts to effect reaction between GeH_2 and acetylene or diphenylacetylene at −63°, in analogy with the high-temperature reactions of GeI_2,[8] were unsuccessful.

We have observed that no reaction occurs when both the digermane and the ammonia are completely in the gas phase; however, reaction proceeds in the presence of even traces of liquid ammonia. The basic catalyst is ammonia itself and not the amide ion because the reaction goes without noticeable change in 1 *M* ammonium nitrate–liquid ammonia solution. Apparently, relatively weak bases cause the disproportionation of digermane. In addition to ammonia and those bases shown to be effective by Bornhorst and Ring,[1] aqueous sodium hydroxide causes the disproportionation.[4,9]

Acknowledgment.—This work was supported by the United States Atomic Energy Commission.

[8] M. E. Volpin, *et al.*, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2067 (1963).

[9] R. Dreyfuss, unreported observations.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
IOWA STATE UNIVERSITY, AMES, IOWA 50010

Kinetic Studies of Amine Substitution in Aminopentacarbonyltungsten(0) Complexes

BY CAROL M. INGEMANSON AND ROBERT J. ANGELICI

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Kinetic and mechanistic studies of CO substitution in metal carbonyl complexes have been conducted on numerous systems.[1] Yet relatively little effort has gone into studies involving the substitution of other groups which might also be present in the complex. It was the purpose of the present investigation to examine the rates and mechanisms of amine displacement from $(Am)W(CO)_5$ according to

$$(Am)W(CO)_5 + L \longrightarrow (L)W(CO)_5 + Am \quad (1)$$

The rate of this reaction was investigated as a function of the basicity of the primary, secondary, and tertiary amines and also of the nucleophilicity of the phosphine or phosphite, L.

Experimental Section

Preparation and Purification of Materials.—The ligands, L, and solvents were purified as given elsewhere.[2] The $(Am)W(CO)_5$ complexes were prepared by the method of ultraviolet irradiation of a tetrahydrofuran solution of $W(CO)_6$ and the desired amine. Most of the complexes had been prepared previously[3] and were identified by their infrared spectra. In addition, satisfactory C, H, and N analyses were obtained for the complexes $((CH_2)_5NH)W(CO)_5$, $((CH_3)_3N)W(CO)_5$, and $(O(CH_2CH_2)_2NH)W(CO)_5$. The products, $(L)W(CO)_5$, of reaction 1 were identified by their uv–visible and infrared spectra which were identical with those of $(L)W(CO)_5$ complexes prepared and

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[1] For a recent review, see R. J. Angelici, *Organometal. Chem. Rev.*, **3**, 173 (1968).

[2] R. J. Angelici and C. M. Ingemanson, submitted for publication

characterized independently.[3] Attempts to measure the rates of piperidine replacement from the chromium and molybdenum analogs, $((CH_2)_5NH)Cr(CO)_5$ and $((CH_2)_5NH)Mo(CO)_5$, however, showed that significant CO substitution occurred leading to products of the type $(L)_2M(CO)_4$.

Kinetic Measurements.—The uv–visible spectra of the yellow $(Am)W(CO)_5$ complexes in decalin solvent show an absorption at 410 mμ with a shoulder at 445 mμ, in addition to very intense bands at 235 and 286 mμ. During the reaction of $(Am)W(CO)_5$ with L, the solution becomes colorless and its spectrum corresponds to that of $(L)W(CO)_5$ which absorbs light only very slightly at 410 mμ. For this reason, the rate of $(Am)W(CO)_5$ disappearance was followed by noting the decrease in absorbance at 410 mμ. Since concentrations of L were at least 10 times that of the complex, plots of $\ln (A - A_\infty)$ *vs.* time, where A is the absorbance at any given time and A_∞ is the absorbance at the end of the reaction, gave slopes which were pseudo-first-order rate constants, k_{obsd}, for the reaction. The dependence of these pseudo-first-order rate contants on the concentration of L is

$$k_{obsd} = k_1 + k_2[L] \qquad (2)$$

A least-squares computer program was used in the evaluation of k_1 and k_2 from k_{obsd} and [L] data. These rate constants are presented in Table I.

TABLE I

RATE CONSTANTS (k_1 AND k_2) FOR THE REACTION OF $(Am)W(CO)_5$ WITH L IN DECALIN SOLVENT AT 80.4°

		L					
Am	10^5k_1	$P(n\text{-}C_4H_9)_3$ 10^3k_2	$P(O\text{-}n\text{-}C_4H_9)_3$ 10^3k_2	$P(OCH_2)_3CC_2H_5$ 10^3k_2	$P(C_6H_5)_3$ 10^3k_2	$P(OC_6H_5)_3$ 10^3k_2	$As(C_6H_5)_3$ 10^3k_2
$O(CH_2CH_2)_2NH$ (8.3)[b]	17.1[c]	58.8[a]	14.7[a]	9.07[a]	1.93[a]	2.28[a]	1.68[a]
NH_3 (9.2)[b]	54.7	55.8	19.3	11.4	7.71	1.58	...
$(CH_3)_3N$ (9.7)[b]	17.1	55.0	6.87	4.25	0	1.35	0
CH_3NH_2 (10.6)[b]	8.12	27.6	11.3	13.2	3.88	1.87	1.15
$(CH_3)_2NH$ (10.8)[b]	5.19	67.1	17.1	6.85	1.10	0.493	0.713
$(CH_2)_5NH$ (11.1)[b]	1.31	31.1	2.91	1.29	0.191	0.091	0.131
C_5H_5N (5.2)[b]	4.61	15.6	3.81	1.86	0.53	0.30	0.61

[a] k_2 values in units of M^{-1} sec^{-1}. [b] pK_a values: D. D. Perrin, "Dissociation Constants of Organic Bases in Aqueous Solutions," Butterworth and Co. Ltd., London, 1965. [c] k_1 values in units of sec^{-1}.

The kinetic studies were carried out in a foil-wrapped, two-legged, glass reaction vessel which was fitted with a side-arm stopcock permitting the maintenance of a nitrogen atmosphere during the reaction.[4] The top of the vessel was fitted with a septum. Prior to a run a freshly prepared 20-ml solution of approximately 2×10^{-4} M complex was pipetted into one leg of the vessel and 20 ml of a 25–350 $\times 10^{-4}$ M ligand, L, solution into the other. After equilibrating for about 15 min in the constant-temperature bath (±0.05°), the reactant solutions were thoroughly mixed by tilting the vessel. Samples of the solution were withdrawn at appropriate time intervals and their intensities at 410 mμ examined on a Beckman DB-G spectrophotometer.

In the absence of L, the $(Am)W(CO)_5$ complexes decompose at rates which are almost as fast as their reaction with L. One of the decomposition products is $W(CO)_6$ which can be readily identified by its strong infrared absorption at 1984 cm^{-1}. Thus during the thermostating period of the kinetic studies some $W(CO)_6$ does form, but this does not absorb at 410 mμ and does not affect the rate of reaction. If $(Am)W(CO)_5$ and L are mixed immediately and then thermostated at the higher temperatures, no $W(CO)_6$ is produced, and the rate is the same as observed by the other procedure. Hence in the presence of L, $(L)W(CO)_5$ is the only product and no decomposition of $(Am)W(CO)_5$ occurs.

Results and Discussion

The rate of reaction of $(Am)W(CO)_5$ with L according to eq 1 obeys the rate law

$$\text{rate} = k_1[(Am)W(CO)_5] + k_2[(Am)W(CO)_5][L]$$

The values of k_1 (in sec^{-1}) calculated from eq 2 and given in Table I are averages of those obtained with different L groups. Generally the k_1 value for a given L group was within 10% of the averages listed in the table. This was true for all ligands except $P(n\text{-}C_4H_9)_3$, and sometimes $P(O\text{-}n\text{-}C_4H_9)_3$, which were 50–100% larger than the average. The reason for these discrepancies is not known. The k_1 term in the rate law is assumed to correspond to an SN1 mechanism wherein the rate-determining step is the breaking of the W–N bond in $(Am)W(CO)_5$ to give a five-coordinated intermediate which rapidly reacts with L to give the product $(L)W(CO)_5$. Such a mechanism would predict that the rate constants would depend significantly upon the strength of the W–Am bond. That k_1 decreases as $NH_3 > O(CH_2CH_2)_2NH = (CH_3)_3N > CH_3NH_2 > (CH_3)_2NH > (CH_2)_5NH$ suggests that the basicity (pK_a) is important in determining the rate of Am dissociation. With the exception of NH_3, which reacts much faster than its pK_a would suggest, the rates of dissociation increase with decreasing basicity of the amine. Another indication of this trend was obtained from qualitative studies of amine displacement from $(p\text{-}CH_3OC_6H_4NH_2)W(CO)_5$. The low p$K_a$ (5.3) of $p\text{-}CH_3OC_6H_4NH_2$ would suggest that it should react very fast, and, indeed, it reacted much too fast to study at 80.4°. Reasonable rates could be achieved at 35°. The trend in increasing rate of Am dissociation with decreasing basicity of Am is not surprising, since it has been shown in equilibrium studies[2] of $(Am)W(CO)_5$, where Am is a substituted aniline, that the more weakly basic anilines are displaced more completely than those which are stronger bases. In contrast to the anilines, however, pyridine (Table I) is not rapidly substituted in $(C_5H_5N)W(CO)_5$ despite its low pK_a (5.2). It appears that pyridine is more tightly bonded to the tungsten than an amine of the same basicity.

The k_2 term in the rate law implies that the reaction also takes place by an SN2 mechanism, in which L attacks the complex to perhaps form a seven-coordinated transition state or intermediate. The relative values of k_2 decrease in the order: $P(n\text{-}C_4H_9)_3 > P(O\text{-}n\text{-}C_4H_9)_3 > P(OCH_2)_3CC_2H_5 > P(C_6H_5)_3 \sim P(OC_6H_5)_3 \sim As(C_6H_5)_3$. This is the generally observed trend of nu-

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(3) R. J. Angelici and M. D. Malone, *Inorg. Chem.*, **6**, 1731 (1967).

(4) R. J. Angelici and J. R. Graham, *ibid.*, **6**, 988 (1967).

cleophilicities[1,5] of these ligands toward many metal carbonyl complexes and is essentially the same as that obtained for the reaction of L with $W(CO)_6$ to form $(L)W(CO)_5$.[6]

At 60.0, 70.0, and 92.0°, the values of k_1 for the reaction of $(O(CH_2CH_2)_2NH)W(CO)_5$ with $P(C_6H_5)_3$ were 1.56, 4.11, and 30.0×10^{-5} sec^{-1}, respectively. At the same temperatures k_2 increased as follows: 0.42, 1.21, and 8.69×10^{-3} M^{-1} sec^{-1}. From the k_1 results, $\Delta H_1{}^*$ and $\Delta S_1{}^*$ were calculated to be 22.5 kcal/mol and −13 eu, respectively. The negative value of $\Delta S_1{}^*$ is somewhat surprising for an SN1 reaction, although there are SN1 reactions of other metal carbonyls[1] which have entropies of activation as low as −10 eu. It should be noted that $\Delta H_1{}^*$ is much lower than that observed[6] for the dissociation of CO from $W(CO)_6$, which is in general agreement with lower solution stability of $(Am)W(CO)_5$ as compared to $W(CO)_6$. For the k_2 term, $\Delta H_2{}^*$ and $\Delta S_2{}^*$ are 21.0 kcal/mol and −11 eu, respectively. In this case, the entropy of activation is quite normal for reactions proceeding according to an SN2 mechanism.

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CONTRIBUTION FROM THE CHEMICALS DIVISION,
OLIN MATHIESON CHEMICAL CORPORATION,
NEW HAVEN, CONNECTICUT 06504

Novel Synthesis Routes to Chlorine and Bromine Pentafluorides

BY GENE A. HYDE AND MAX M. BOUDAKIAN

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The reaction of alkali chlorides and bromides with fluorine (at atmospheric pressure) was first studied by Moissan.[1] With chloride salts, chlorine and the alkali fluoride were produced. Under the same conditions, bromine trifluoride and potassium fluoride were formed from potassium bromide and fluorine.[2]

Asprey, Margrave, and Silverthorn,[3] Bode and Klesper,[4-6] and Kelly, Post, and Mason[7] have reported the fluorination of alkali chlorides to give alkali tetrafluorochlorates, $MClF_4$ (M = K, Rb, Cs), at temperatures of 90–300° and pressures up to 4000 atm. Asprey, *et al.*,[3] also obtained alkali tetrafluorobromates, $MBrF_4$ (M = K, Rb, Cs) from the fluorination of the corresponding alkali metal bromides under similar conditions. In none of these investigations was the composition of the final gas phase investigated.

We now wish to report that under the proper conditions chlorine or bromine pentafluoride may be obtained by fluorination of the respective potassium halide

$$3F_2 + KX \longrightarrow XF_5 + KF \quad (X = Cl \text{ or } Br)$$

Chlorine pentafluoride has been prepared from fluorine and chlorine trifluoride with either thermal[8] or ultraviolet[9] activation, by the reaction of platinum hexafluoride and chlorine trifluoride,[10] by fluorination of tetrafluorochlorate salts,[11] directly from the elements by electric discharge,[11] and, by an electrolytic process, from chlorine or chlorine trifluoride and hydrogen fluoride.[12] Trace amounts have also been reported from the action of krypton difluoride on the silver chloride windows of an infrared cell.[13]

Bromine pentafluoride has been prepared by direct fluorination of bromine or bromine trifluoride.[14,15]

We have found the procedure described herein to be most convenient for the laboratory preparation of chlorine or bromine pentafluoride since the starting materials are easily obtainable and the products are almost completely free of the trifluorides and other impurities.

By this procedure, we have made many preparations of chlorine pentafluoride and have established the following optimum conditions (figures in parentheses indicate the ranges investigated): F_2:KCl mol ratio, 5:1 (3:1–12:1); temperature, 200° (100–300°); time, 8 hr (4–112 hr). These conditions gave an average in-hand yield, based on KCl charged, of 65.0 ± 4.7% (95% confidence limits). The particle size of the KCl (75 or 350 μ) had no apparent effect on the yield.

Other chlorides can also be fluorinated under similar conditions to give chlorine pentafluoride: NaCl (240°, 4 hr, 55.6% yield); $BaCl_2$ (240°, 64 hr, 7.1% yield).

The parameters of the bromine pentafluoride preparation were not as thoroughly investigated. However, yields of 47%, based on potassium bromide charged, were obtained with an F_2:KBr mole ratio of 5.8:1, at 25° for 16 hr.

Experimental Details

Materials.—Solid reagents (analytical grade) were dried in a vacuum oven at 120°. Fluorine, obtained from Allied Chemical Corp., was passed through a hydrogen fluoride scrubber before use. Reactors were Hoke stainless steel or Monel cylinders with Hoke Monel needle valves (M324A).

Precautions.—*Preparations involving more than 0.25 mol of potassium chloride in a 1-l. stainless steel cylinder (rated at 1800 psi)*

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