Reactions of co-ordinated boron compounds in the gas phase. Part I. Borine carbonyl and trimethylamine

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Alberto E Villa
University of Chile
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The complexes formed between pyridines and cadmium halides are in marked contrast to those formed with zinc. The complexes isolated from solution contain up to six molecules of base to each metal atom and a wide range of complexes results on heating these complexes. Bis-pyridinecadmium bromide has an octahedral arrangement of co-ordinating groups around each metal atom [14] and $Cd_3py_2Cl_6$, $CdpyBr_2$, $Cd(\beta\text{-pic})Cl_2$, and $Cd(\beta\text{-pic})Br_2$ are isomorphous with the corresponding manganese [2] complexes, whilst $Cd(\gamma\text{-pic})_4Cl_2$ is isomorphous with the corresponding cobalt and nickel [4] derivatives. There is, therefore, strong evidence for octahedral co-ordination about the metal in most of the cadmium complexes and this is in agreement with the infrared evidence for these derivatives since no bands which can be assigned to metal–halogen modes are observed above 200 cm.$^{-1}$.

Complexes of metal(II) halides with pyridines have now been prepared for all the metals from chromium to zinc and also for cadmium. Of these metals, complexes of type MLX_2 and $M_3L_2X_6$ could be prepared for manganese, cobalt, nickel, and cadmium by thermal decomposition of the complexes containing larger amounts of ligand. All the latter derivatives have octahedral co-ordination about the metal. The lack of similar complexes of chromium and iron may well be due to oxidation during the thermal decomposition process. Copper(II) complexes all have very distorted octahedral co-ordination because of the Jahn–Teller effect and the zinc halide complexes with pyridines seem to show particular preference for tetrahedral co-ordination and even zinc(II) chloride has a tetrahedral arrangement of halogen atoms about the metal.[15] Copper and zinc, which do not form regularly octahedrally co-ordinated species, do not form the intermediate phases described above.

[14] T. I. Malinovskii and Y. A. Simonov, *Doklady Akad. Nauk S.S.S.R.*, 1962, **147**, 96.

EXPERIMENTAL

The complexes prepared are listed in Table 1. The methods of preparation are as follows:

A. The hydrated metal(II) halide was suspended in ether and a solution of the pyridine in ethanol added to the boiling ethereal suspension. The precipitated adduct was filtered off, washed with ether, and dried.

B. These were prepared by thermal decomposition of the preceding complex in Table 1. Thermal decompositions were investigated on a Stanton Thermal Balance working at a chart speed of 6 in./hr. and samples were subsequently prepared by heating complexes to a pre-arranged temperature in an oven.

C. The hydrated halide was dissolved in ethanol and ligand was added to the solution. The precipitate was filtered off, washed with ether, and dried.

D. As in method *C*, except that it was necessary to add ether to the solution to precipitate the complex. $Cupy_6Br_2$ resulted from the direct interaction between copper(II) bromide and pyridine in this manner but if the precipitate was exposed to moist air $Cupy_2Br_2,2H_2O$ resulted.

E. The metal(II) halide was dissolved directly in the ligand and the complex crystallised on cooling.

F. As method *C* except that methanol was used as the initial solvent.

Reflectance spectra were taken on a Hilger Uvispek Spectrophotometer. Infrared spectra were recorded as Nujol Mulls on a Perkin-Elmer Model 125 Spectrophotometer, and a Grubb–Parsons D.M.2 Spectrophotometer. All samples were examined by X-ray powder photography using a 9 cm. camera and Cu-K_α radiation.

[15] A. F. Wells, " Structural Inorganic Chemistry," 3rd edn., Oxford University Press, 1962.

Reactions of Co-ordinated Boron Compounds in the Gas Phase. Part I. Borine Carbonyl and Trimethylamine

By J. Grotewold, E. A. Lissi, and A. E. Villa

The reaction between borine carbonyl and trimethylamine has been studied from 207·3 to 273·2° K. Below 273·2° K the reaction is second-order: $d(CO)/dt = k(BH_3CO)(Me_3N)$. The Arrhenius parameters associated with this S_N2 reaction are $E = 8·60 \pm 0·30$ kcal./mole, and $A = 10^{9·82 \pm 0·27}$ c.c./mole sec. At 273·2° K the unimolecular rupture of the B–C bond becomes important as a rate-controlling step.

THE kinetics of gaseous reactions such as (1), R and R' being two compounds which can undergo co-ordination

$$RBH_3 + R' = R'BH_3 + R \qquad (1)$$
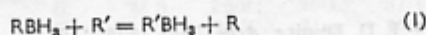
with borine, have been little investigated. These systems, however, offer interesting possibilities such as the study of the kinetic parameters of the second-order nucleophilic substitution if the reaction proceeds in one step by the bimolecular reaction (1), and the isolation of the reaction leading to unimolecular rupture of the co-ordinated boron–base bond if the reaction proceeds in two steps, (2) and (3) [reaction (2) is then rate-determining]. The mechanism will depend upon the relative

$$RBH_3 = R + BH_3 \qquad (2)$$

$$BH_3 + R' = R'BH_3 \qquad (3)$$

stability of the adducts, the temperature, the concentration of amine, the steric hindrance to the bimolecular reaction, etc. Consequently, the prediction of the effective mechanism is difficult, since very little is known about reactions of this type.[1,2] Nevertheless, the systems have the advantage that it is easy to differentiate experimentally between the mechanisms, and, if they compete, to evaluate the two rate constants. The reaction system borine carbonyl–trimethylamine was selected because of its experimental simplicity and the stability of the borine–trimethylamine adduct (H_3B,NMe_3) in comparison with borine carbonyl, although qualitative data[3] on the decomposition of borine carbonyl in the presence of trimethylamine could be interpreted as a process controlled by unimolecular rupture of the B–C bond. A more complete study of this system may help in the elucidation of the mechanism of the thermal decomposition of BH_3CO which has been a matter of controversy.[4]

EXPERIMENTAL

Borine carbonyl was prepared by the original technique[3] with slight modifications. The reaction products were degassed in a conventional high-vacuum line, to eliminate the excess of carbon monoxide, and fractionated at low temperature to eliminate most of the unreacted diborane. Borine carbonyl was then stored at liquid–nitrogen temperature between mercury cut-offs. Its purity was checked by infrared spectroscopy;[5] diborane was the only impurity detected, its presence having no effect on the results.

Trimethylamine (Fluka, " purissimus ") was purified by trap-to-trap distillation, and only the middle fraction used; its purity was checked chromatographically.

Matheson instrumental grade propane was added to all runs, in order (a) to make possible variations in the total pressure independently of the concentration of the reactants, and (b) to act as thermal " buffer " for the heat evolved in the reaction.

Three Pyrex glass reaction vessels of approx. 40 c.c. capacity closed with Teflon O-rings were employed; one was specially designed in order to avoid mixing of reactants in the condensed phase during the charging process. Working temperature was achieved by complete immersion of the reaction vessels in slush baths of fixed melting points, thus eliminating dead-space. The temperature profile was measured with thermocouples and found to be nearly constant.

The rate of reaction was followed by measuring noncondensable products with a calibrated mercury Toepler pump attached to the reaction vessel. It was proved, by chromatography on molecular sieves and differential adsorption on alumina at −197°, that the only noncondensable product was carbon monoxide.

The initial pressure of borine carbonyl was not used in the calculations, to avoid errors arising from the fraction of

diborane present and the borine carbonyl decomposition during the charge process. The initial concentration of the reactant was therefore evaluated from the carbon monoxide accumulated at " infinite " time. This was achieved by leaving the system for a few minutes at room temperature.

Experimental Procedure. Both reactants and propane were carefully degassed before and after the charging process. The reaction was then started by immersing the reaction vessel in the temperature-controlled bath. Equilibrium temperatures, measured by a thermocouple attached to the wall of the reaction vessel, were attained in approximately 15 sec. This time lag did not influence appreciably the determination of the rate constants, as discussed in the next section. Besides, only a small portion of the reaction vessel was at liquid-nitrogen temperature before immersion of the vessel in the thermostat bath. The reaction was stopped by immersion of the vessel in liquid nitrogen, and carbon monoxide was pumped out and measured in the Toepler pump; the carbon monoxide was not returned to the reaction vessel. The reaction was then started again, this procedure being repeated until *ca.* 70% conversion was reached.

Questions regarding effectiveness of mixing, secondary reactions, surface effects, reactions in condensed phase, and carbon monoxide occlusion were experimentally checked and are discussed in the next section.

RESULTS

The reaction system can be represented by the elementary steps (4)—(6). The Me_3N,BH_3 appeared as a white solid.

$$BH_3CO + Me_3N = CO + Me_3N,BH_3 \quad (4)$$

$$BH_3CO = BH_3 + CO \quad (5)$$

$$BH_3 + Me_3N = Me_3N,BH_3 \quad (6)$$
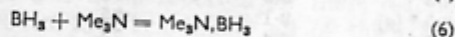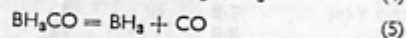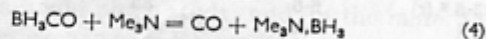
Since all runs were carried out in an excess of amine, the reaction can be treated as " pseudo-unimolecular " regardless of the relative importance of reactions (4) and (5). If reaction (6) is much faster than reaction (5), or any other reaction of borine, the kinetic rate law is

$$d(CO)/dt = k_4(BH_3CO)(Me_3N) + k_5(BH_3CO) \quad (7)$$

and putting

$$k' = k_4(Me_3N) + k_5 \quad (8)$$

we get

$$d(CO)/dt = k'(BH_3CO) \quad (9)$$

Experimental results expressed as $k'/(Me_3N)$ are shown in the Table. Most of the values of $k'/(Me_3N)$ are averages of values from the same run calculated for consecutive time intervals from equation (10), where $(BH_3CO)_{t_i}$ is obtained from the carbon monoxide evolved from t_1 to t_∞. The

$$k' = \{1/(t_2 - t_1)\} \ln \{(BH_3CO)_{t_1}/(CO)_{t_2}\} \quad (10)$$

values of k' so obtained were divided by the average concentration of trimethylamine in the time interval t_1 to t_2. This average concentration was obtained from the initial concentration of the amine and corrected for the amount of diborane present at t_0 and the amount of carbon monoxide evolved during the run in the time interval t_0 to t_1.

[1] A. C. Rutenberg, A. A. Palko, and J. S. Drury, *J. Amer. Chem. Soc.*, 1963, **85**, 2702; *J. Phys. Chem.*, 1964, **68**, 976; A. C. Rutenberg and A. A. Palko, *ibid.*, 1965, **69**, 527.
[2] H. Brumberger and R. A. Marcus, *J. Chem. Phys.*, 1956, **24**, 741; R. W. Parry and T. C. Bissot, *J. Amer. Chem. Soc.*, 1956, **78**, 1525; W. Dutton, W. G. Paterson, and M. Onyszchuk, *Proc. Chem. Soc.*, 1960, 149; T. D. Coyle, *ibid.*, 1963, 172.

[3] A. B. Burg and H. I. Schlesinger, *J. Amer. Chem. Soc.*, 1937, **59**, 780.
[4] M. E. Garabedian and S. W. Benson, *J. Amer. Chem. Soc.*, 1964, **86**, 176; T. P. Fehlner and W. S. Koski, *ibid.*, 1965, **87**, 409.
[5] R. D. Cowan *J. Chem. Phys.*, 1950, **18**, 1101.

Mixing of Reactants. Incomplete mixing of reactants can arise from a differential rate of evaporation at the beginning of the reaction. This should yield errors in the rate-constant values if the time of mixing were of the order of the reaction time. The measured rate of reaction would be then, to some extent, diffusion-controlled. This is not the case in the present experimental conditions, as can be deduced from the following facts. (1) The rate constants are independent of contact times for the two temperatures that involve the shortest contact times. (2) The rate

Experimental values of $k'/(Me_3N)$

$10^7[Me_3N]$ (moles c.c.$^{-1}$)	$10^7[BH_3CO]$ (moles c.c.$^{-1}$)	$10^7[Propane]$ (moles c.c.$^{-1}$)	$10^{-2}k'/[Me_3N]$ (c.c. mole^{-1} sec.$^{-1}$)
At 207·3° K			
5·4	2·2	100	0·070
5·9	4·1	110	0·053
8·3	2·1	95	0·071
8·8	4·9	97	0·060
10·1	3·6	100	0·085
			Av. 0·068 ± 0·006
At 222·1° K			
2·7	2·9	147	0·318
7·6	4·7	147	0·260
15·0	7·4	147	0·262
19·1	6·6	147	0·239
25·8	7·4	147	0·292
			Av. 0·274 ± 0·011
At 245·2° K			
5·4	1·05	110	1·42
12·3 *	4·3	100	1·18
21·7 *	3·0	100	0·82
23·5 * (c)	6·6	85	1·54
25·1	4·4	88	1·23
32·3 * (b)	7·2	85	1·46
39·5	3·9	78	1·28
43·5 * (a)	9·1	85	1·54
44·5 *	6·4	72	1·43
47·0 *	6·1	85	1·50
48·0 *	6·1	85	1·15
54·0 *	6·6	85	1·19
60·5 * (d)	7·7	64	1·32
66·1 * (e)	7·7	195	1·25
77·2 * (f)	10·0	55	1·25
			Av. 1·30 ± 0·05
At 273·2° K			
1·55 †	0·83	156	28
2·60 †	1·4	155	19
4·20 †	3·7	150	26
5·15	5·3	150	26·3
7·10	1·8	155	18·9
7·30 †	4·2	130	13·4
9·30	3·1	155	14·8
9·70 †	7·4	130	12·6
15·5 †	4·0	125	12·9
16·0	4·1	142	10·3
17·4 *	1·1	55	11·5
18·9 *	7·8	150	9·4
24·7 *	3·3	55	11·5
25·8	5·6	155	11·0
27·9	2·8	155	14·9
28·0 *	3·9	55	9·7
34·2 †	6·7	120	10·7
38·0 †	3·7	115	13·5
51·5 *	10·5	55	10·0

Errors quoted are the standard errors of the mean.

* Runs carried out in a spherical vessel. † Reaction vessel coated with paraffin wax.

constants are independent of the shape of the reaction vessels. Runs labelled with an asterisk in the Table were carried out in a spherical vessel; other runs were done in cylindrical reactors that would magnify mixing problems.

(3) The rate constants were independent of the initial distribution of reactants. The initial determination of each run was started with the reactants separated in the condensed phase, with consequent increase of the chance for selective evaporation to occur. The subsequent determinations were started with the reactants mixed in the condensed phase. The results were not sensitive to the initial distribution. (4) The more direct proof that the rate of reaction is not affected by diffusion problems is obtained from the values of the rate constants obtained for runs (d), (e), and (f) of the Table. These runs were done at different propane pressures (and hence different total pressure) with no appreciable variation in rate constants. The same conclusion can be reached from inspection of the runs carried out at 273·2°. (5) Resolution of the mass transport equation was accomplished at the lowest temperature under the most unfavourable contour conditions (the three reactants in separate layers). The calculations were done with and without consideration of chemical reaction. It can be concluded that (i) the gradient arising from chemical reaction is negligible, and (ii) homogeneous distribution is reached in a much shorter time than contact times; the combined effects of these two factors would influence k' values by not more than 5%.

Secondary Reactions. Secondary reactions affecting the mechanism coming from the system itself or from impurities can be neglected on the following basis. (a) Runs (a), (b), and (c) were carried out without changing both propane and amine, fresh borine carbonyl being added to the reaction vessel. In this case it can be seen that the constancy of the ratio $k'/(Me_3N)$ shows that there are no complications arising from impurities in the reactants. (b) Values of $k'/(Me_3N)$ calculated from equation (10) do not show any trend with conversion (up to *ca.* 70%). (c) Values presented in the Table for the three lower temperatures are independent of the concentration of amine and borine carbonyl. Then it can be concluded that there are not secondary reactions on borine carbonyl. Furthermore, the estimation of the rate of reaction of borine with borine carbonyl [4] shows that this reaction must be much slower than reaction (6). (d) A run carried out without amine evolved no carbon monoxide after 15 minutes at 245·2° K. (e) Diborane formation by reactions with solid products will not alter the results because diborane reacts immediately with amine under the present conditions.[3]

Surface Effects. Reproducible results were obtained at temperatures lower than 273·2° K provided that some solid product was formed and kept in the reaction vessel. This requirement was fulfilled if the reaction vessel was not evacuated further than 0·1 torr between two consecutive runs. Runs (a), (b), and (c) show that the rate constants were unaffected by the increasing amount of solid present. At 273·2° K the surface ageing became more important, but reproducibility was easily obtained when the internal walls of the reaction vessel were covered with a thin layer of paraffin wax. Runs carried out under these conditions are labelled (†) in the Table.

Reactions in Condensed Phase, Carbon Monoxide Occlusion, and Attainment of Equilibrium Temperature. These factors can be disregarded, since the values of k' obtained by application of equation (10) were not sensitive to the time interval $(t_2 - t_1)$. These time intervals varied from 60 to 420 sec. at 273·2° K, and from 240 to 1300 sec. at 245·2° K, with no appreciable effect on the values of k'. Furthermore, when all the carbon monoxide was pumped

out after one measurement, the system did not yield any additional carbon monoxide if the reactor was immersed in a bath at 195° K for a few minutes.

DISCUSSION

If the values of k' are plotted against the concentration of trimethylamine, for a single temperature, the values of k_4 and k_5 can be obtained from the slope and the intercept, respectively. If this is done for the experimental data in the Table, at the three lower temperatures the intercept is zero within experimental error. This means that $k'/(Me_3N)$ is independent of the amine concentration, as shown in the Table. It can then be concluded that at 207·3°, 221·1°, and 245·2° K the reaction system obeys the kinetic expression

$$d(CO)/dt = k(BH_3CO)(Me_3N) \qquad (11)$$

where $k = k'/(Me_3N)$ can be identified as k_4, the bimolecular rate constant.

The values of $k'/(Me_3N)$ at 273·2° K show a strong dependence on amine pressure when this is lower than 12 torr. This fact can be related to the production of carbon monoxide by a first-order mechanism as represented by reactions (5) and (6). Furthermore, the increased sensitivity to the wall treatment would be explained if reaction (5) were heterogeneous on a clean surface.

The kinetic behaviour of the system is described by equation (7) only if reaction (6) is much faster than any other reaction of borine within the system. This assumption is supported by the fact that the concentration of trimethylamine is much larger than the concentration of any other compound that might react with borine, and also by the high rate-constant values found [6] for reactions which are similar to reaction (6).

Least-squares treatment of the k' values as a function of amine concentration at 273·2° K gave the following values: $k_4 = 1003 \pm 74$ c.c./mole sec.; $k_5 = 4·01 \pm 1·65 \times 10^{-4}$ sec.$^{-1}$.

Since the unimolecular contribution at 273·2° K is small, the value of k_5 cannot be determined accurately, but its order of magnitude is in agreement with more precise values obtained in this laboratory [7] using triethylamine as scavenger of BH_3.

The kinetic parameters obtained by a least-squares treatment are: $E_4 = 8·60 \pm 0·30$ kcal./mole; $A_4 = 10^{9·82 \pm 0·27}$ c.c./mole sec.; $\Delta S_4^{\ddagger} = -13·25$ cal. deg.$^{-1}$ mole^{-1}.

A S_N2 mechanism seems to be plausible for the bimolecular reaction. It involves an inversion on the central boron atom. The reaction can then be represented as where the three hydrogen atoms attached to
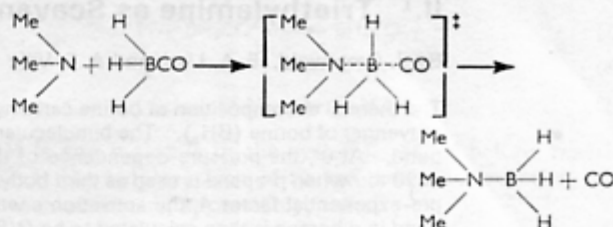
the boron atom are nearly planar in the activated complex. The value of the pre-exponential parameter obtained is of the order predicted by the absolute rate theory for this type of reaction.[8]

From the rate constant obtained for reaction (4), and the values for the enthalpic and entropic changes [9,10] associated with this reaction, it can be derived that for reaction (12)

$$CO + Me_3N,BH_3 = BH_3CO + Me_3N \qquad (12)$$
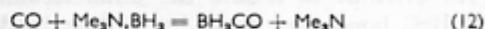
in the gaseous phase

$$\log k_{12} \text{ (c.c mole}^{-1} \text{ sec.}^{-1}) = 10·92 - (21,300/2·3RT)$$

Reactions involving displacement on boron atoms have also been studied.[1,11] It is difficult, however, to compare our values of the Arrhenius parameters with either Rutenberg's [1] or Brownstein's.[11] Their values come from a liquid-phase study, and, furthermore, they only consider exchange of BF_3 or BCl_3 groups, not BH_3. The energies of activation reported for these reactions range from 1·8 to 13·2 kcal./mole, all of them being related to weaker bonds than B–C or B–N bonds. The effect of replacing the hydrogen atoms by halogen atoms should have two effects upon the activation energies, other than those arising from changes in bond strength, due to (a) higher repulsion energies between the reactants, and (b) changes in rearrangement energies of the boron atom to reach the configuration of the activated complex.

On the other hand, the A-factors associated with these reactions range from $10^{5·9}$ to $10^{15·9}$ c.c./mole sec. They do not seem to be comparable with the values for bimolecular reactions in the gas phase. The effects of basic and steric factors on this type of reaction are now being studied.

DEPARTMENT OF INORGANIC CHEMISTRY,
FACULTAD DE CIENCIAS EXACTAS Y NATURALES,
UNIVERSIDAD DE BUENOS AIRES,
PERÚ 222, BUENOS AIRES, ARGENTINA.
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