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SCRAMBLING REACTIONS BETWEEN BORON AND VARIOUS PHOSPHORUS MOIETIES: THE $B(NEt_2)_3/PCl_3$, $B(NEt_2)_3/OPCl_3$ AND $B(NEt_2)_3/SPCl_3$ SYSTEMS

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Abstract—A ^{31}P, ^{11}B and ^{1}H NMR study of the scrambling reactions between tris (diethylamino) boron $B[N(C_2H_5)_2]_3$ and PCl_3, $OPCl_3$ and $SPCl_3$ shows that the mixed species $QCl_{3-n}(NEt_2)_n$ [Q = B, P, OP or SP and n = 1 or 2] are more favoured than would be the case if a completely random mechanism was involved. In the $PCl_3/B[N(C_2H_5)_2]_3$ system the chlorine substituents display preferential affinity for phosphorus moieties over boron centers while the reverse situation is encountered in the two other systems involving quadruply coordinated phosphorus. The Lewis acidity of boron and the effective electronegativity of phosphorus moieties may explain these trends.

INTRODUCTION

In previous work[1–5] we employed NMR spectroscopy (^{1}H and ^{11}B) to realize a quantitative study of scrambling reactions between monofunctional (–F, –Cl –Br, –I, –SCN, $-C_3H_7$ $-OCH_3$, $-N(CH_3)_2\cdots$) or difunctional (–O–) substituents and tri or tetrafunctional boron moieties. The results obtained permit the assumption that, in the absence of steric constraints, the equilibrium distribution of the various species is very largely determined by the back-coordination possibilities between substituent and the boron centre. In view of this it seemed interesting to confront two different central atoms such as boron and phosphorus, for example BX_3 and PY_3. The choice of the system, that is to say the selection of the substituents X and Y, is quite delicate; many combinations not only undergo redistribution but also complexation reactions and even decomposition. The system $B(NEt_2)_3/PCl_3$ (I), for which the possibilities of redistribution have been mentioned[6] but not studied quantitatively, and the systems $B(NEt_2)_3/OPCl_3$ (II), $B(NEt_2)_3/SPCl_3$ (III) have been chosen as the subject of this investigation.

EXPERIMENTAL

PCl_3, $OPCl_3$ and $SPCl_3$ were obtained commercially and fractionated before use. Tris(diethylamino)boron was made from BCl_3 and Et_2NH in hexane at −70°C, according to literature[7].

For each of the three systems under investigation several samples were prepared by weighing the desired amounts of the chosen ingredients directly in NMR tubes under an argon atmosphere. After sealing the tubes, the samples were maintained at 25°C (I) or 120°C (II and III) and periodically analyzed by ^{31}P and ^{11}B NMR immediately after cooling to room temperature. The approach to equilibrium could be followed by examination of the spectral modifications. For instance in system I, the PCl_3 signal (107 ppm) in the ^{31}P spectrum gradually disappeared while two new signals could be detected at 41 and 49 ppm. Scrambling effects were also noticeable in the ^{1}H and ^{11}B spectra. From the latter we could also infer that no adduct formation involving a B–P coordination bond occurred since such a compound would be characterized by a strong resonance line ($0 < \delta^{11}B < 10$ ppm).

The equilibrium data were obtained long after the spectra ceased to show any further change with time, i.e. 6 hr at 25°C (system I), 20 days at 120°C (systems II and III). Peak assignment in the NMR spectra was achieved on the basis of known chemical shifts and checked by material balance calculations. The assignments are summarized in Table 1. The spectra were measured on Perkin–Elmer spectrometers, model R-10 (^{11}B, ^{31}P) and model R-12 (^{1}H). Chemical shifts are reported in ppm downfield from usual standards: $Et_2O.BF_3$ (external), P_4O_6 (external) and $(CH_3)_4Si$ (internal). The quantitative evaluation of the equilibrium molar distribution was achieved through the usual methods, using a curve analyzor Dupont de Nemours (^{1}H spectra) or weighing copies of spectra (^{11}B and ^{31}P) to evaluate the relative area of the phophorus, boron or methylic protons (N–C–CH_3) signals. Averaged equilibrium constants and related errors were computed as previously reported[8, 9].

RESULTS AND DISCUSSION

When two monofunctional substituents ($X = NEt_2$, Y = Cl) exchange sites between two distinguishable trifunctional central moieties (P, OP or SP and B) 8 species $QX_{3-i}Y_i$ (Q = P, OP, SP or B; i = 0, 1, 2 or 3) are expected to form. Their equilibrium concentrations are completely determined by a set of four independent constants which separately describe the subsystems

Table 1. NMR (^{1}H, ^{31}P, ^{11}B) characterization of the QX_iY_{3-i} species

QX_iY_{3-i}	$\delta^{11}B$(ppm)	$\delta^{31}P$(ppm)	$\delta^{1}H$(ppm) (N–C–CH_3)
$B(NEt_2)_3$	28.7[17]^a	—	0.93[15]
$BCl(NEt_2)_2$	28.4[17]	—	1.05[14]
$BCl_2(NEt_2)$	30.6[17]	—	1.12[14]
BCl_3	46.5[17]	—	—
$P(NEt_2)_3$	—	6[10]	1.01[19]
$PCl(NEt_2)_2$	—	41[10]	1.10[19]
$PCl_2(NEt_2)$	—	49[10]	1.18[18]
PCl_3	—	107[16]	—
$OP(NEt_2)_3$	—	−89.5[20]	1.06[19]
$OPCl(NEt_2)_2$	—	−87.3[20]	1.12[19]
$OPCl_2(NEt_2)$	—	−97.2^b	1.21[19]
$OPCl_3$	—	−110.8[21]	—
$SP(NEt_2)_3$	—	−35.2[22]	1.09[19]
$SPCl(NEt_2)_2$	—	−30.4[20]	1.15[19]
$SPCl_2(NEt_2)$	—	−53.2[20]	1.26[19]
$SPCl_3$	—	−84.2[21]	—

(a) References between brackets. (b) This work.

(BX_3/BY_3; PX_3/PY_3;...) and one "intersystem" constant. The former $(K_i)_Q$ correspond to the disproportionation of the mixed species according to the following scheme:

$$2QX_{3-i}Y_i \rightleftarrows QX_{3-i+1}Y_{i-1} + QX_{3-i-1}Y_{i+1} \quad (i = 1 \text{ or } 2)$$

and

$$(K_i)_Q = [QX_{3-i+1}Y_{i-1}][QX_{3-i-1}Y_{i+1}]/[QX_{3-i}Y_i]^2.$$

Each set of constants may be determined either from the actual system (BX_3/PY_3 for example) or independently from the appropriate subsystem (BX_3/BY_3 or PX_3/PY_3). The intersystem constant K_I determines the distribution of the two kinds of substituents (X and Y) between the two central moieties and, for instance, may be derived from the equilibrium:

$$PX_2Y + BXY_2 \rightleftarrows PXY_2 + BX_2Y$$

$$K_I = [PXY_2][BX_2Y]/[PX_2Y][BXY_2].$$

In the general case, two parameters are needed to describe the overall composition. However they are not independent when the samples under investigation are prepared from only the symmetrical species BX_3 and PY_3 so we make use of only one parameter $R = [Cl]/[B] + [P]$ to define the various mixtures.

Nevertheless in these systems only the concentrations of the four mixed species are used in the calculation of K_I; but in order to describe the affinity of ligands in the overall system we prefer to introduce an affinity constant. For example, with chlorine ligands we shall make use of:

$$Af_{Cl} = \frac{(P-Cl)_r(B-Cl)_s}{(P-Cl)_s(B-Cl)_r}$$

where $(\ )_r$ are the experimental "bond concentrations" and $(\ )_s$ the statistical "bond concentrations".

Af_{Cl} is computed taking into account all the species present in the mixtures. Therefore $Af_{Cl} > 1$ means that chlorine ligands have a preferential affinity towards phosphorus moities. For a random process, Af_{Cl} equals 1.

(1) *The* $B(NEt_2)_3/PCl_3$ *system* (*I*)

A set of 13 sample mixtures were investigated. The overall composition R was varied from 0.5 to 2.5. A selection of the equilibrium molar distributions (C_r) deduced from NMR spectra is reported in the upper part of Table 2A along with the random distribution values (C_s). It is noteworthy that non random behaviour of this system is exemplified by the low concentrations of the symmetrical species which, in several instances, are not detectable at all and, on the other hand, by the rather high concentrations of the mixed species.

The constants $(K_i)_Q$ characterizing the behavior of the subsystems [$PCl_3/P(NEt_2)_3$ and $BCl_3/B(NEt_2)_3$] cannot be evaluated from the experimental data because such an evaluation is only possible if at least 3 of the species ($QX_{3-i}Y_i$, Q = P or B) are simultaneously present in each of these subsystems. This situation does not happen in any mixture investigated in this work. However in 6 samples (R = 1.57; 1.63; 1.74; 1.78; 1.81 and 1.86) there are sufficient quantities of the mixed species (PX_2Y, PXY_2, BXY_2 and BX_2Y) to allow calculation of the "intersystem constant" K_I, the weighted averaged value of which is:

$$\bar{K}_I = 4.4 \pm 0.7 \text{ at } 25°C \quad \text{and} \quad 5.0 \pm 1.0 \text{ at } 120°C.$$

For the affinity constant we obtain:

$$Af_{Cl} = 1.5 \pm 0.4.$$

Keeping in mind that in a random process K_I and $Af_{Cl} = 1$, the actual values show a preferential affinity of chlorine for the phosphorus moieties and of diethylamino groups for the boron centers.

Returning to the two subsystems, the behaviour of the $PCl_3/P(NEt_2)_3$ one is known from a study by Van Wazer *et al.*[10]:

$$(K_1)_P = 4 \times 10^{-7} \quad \text{and} \quad (K_2)_P = 4 \times 10^{-8} \text{ at } 25°C. \qquad (A)$$

Table 2A. Equilibrium data in mol.% in system $B(NEt_2)_3$ vs PCl_3, $SPCl_3$, $OPCl_3$

	QCl_3		$QCl_2(NEt_2)$		$QCl(NEt_2)_2$		$Q(NEt_2)_3$		BCl_3		$BCl_2(NEt_2)$		$BCl(NEt_2)_2$		$B(NEt_2)_3$	
R = [Cl]/[B] + [Q]	C_r	C_s	C_r	C_s	C_r	C_s	C_r	C_s	C_r	C_s	C_r	C_s	C_r	C_s	C_r	C_s
Q = P(25°C)																
1.16[a]	—	2.3[c]	19.0[b]	10.9	27.6	17.0	—	8.9	—	3.6	—	17.0	53.4	26.6	—	13.8
1.57	—	7.3	43.7	20.2	12.1	18.7	—	5.8	—	6.8	15.2	18.7	29.0	17.2	—	5.3
1.63	—	8.5	50.2	21.7	9.5	18.5	—	5.3	—	7.2	21.9	18.5	18.4	15.8	—	4.5
1.74	—	11.3	53.0	24.6	7.5	17.8	—	4.3	—	8.2	26.7	17.8	12.8	12.9	—	3.1
1.78	—	12.1	56.2	25.3	6.4	17.6	—	4.1	—	8.4	27.5	17.6	9.9	12.2	—	2.8
1.81	—	13.0	59.8	25.9	4.7	17.3	—	3.8	—	8.6	26.7	17.3	8.8	11.5	—	2.6
1.86	—	14.8	60.9	27.1	2.7	16.7	—	3.4	—	9.1	29.9	16.7	6.5	10.2	—	2.1
Q = SP (120°C)																
1.16	—	2.3	11.2	10.9	32.7	17.0	—	8.9	—	3.6	16.7	17.0	39.4	26.6	—	13.8
1.35	—	4.1	15.5	15.0	33.0	18.4	—	7.5	—	5.0	22.3	18.4	29.2	22.5	—	9.2
Q = OP(120°C)																
1.30	—	3.4	6.4	13.6	34.9	18.0	—	8.0	—	4.5	32.6	18.0	26.1	23.9	—	10.6
1.40	—	4.9	10.3	16.5	33.5	18.6	—	7.0	—	5.5	35.7	18.6	20.5	21.0	—	7.9
1.75	—	11.3	31.2	24.6	27.6	17.8	—	4.3	—	8.2	38.6	17.8	2.6	12.9	—	3.1

(a) From the ingredients of the mixture as defined. (b) From the NMR data in mol.%. (c) From random substituent redistribution.

Although a characterization of the $BCl_3/B(NEt_2)_3$ system could be deduced from the thermodynamic data[†] of Skinner *et al.*[11]:

$$(K_1)_B = 1.2\times10^{-4} \quad \text{and} \quad (K_2)_B = 1.4\times10^{-11} \quad \text{at } 25°\text{C}, \qquad (B)$$

it was tempting to make a more direct approach by examining the NMR (^{1}H and ^{11}B) spectra of several $BCl_3/B(NEt_2)_3$ mixtures. From the results obtained (see Table 2B) only a lower limit could be estimated

$$(K_i)_B < 5\times10^{-4}.$$

The two sets of values (A) and (B) are in qualitative agreement with the very low amounts of symmetrical species experimentally detected at equilibrium.

The constants $(K_i)_P$, $(K_i)_B$ and K_I may be used to compute the theoretical equilibrium distribution of all species participating in the equilibrium. This has been done for the mixtures for which experimental data were available and a good match of experimental and calculated concentrations is found as long as the overall composition, R, remains lower than 2.

2. *The* $B(NEt_2)_3/SPCl_3$ *system (II)*

Eight sample mixtures characterized by an overall composition ranging from 0.74 to 2.29 were investigated. Again the four mixed species are strongly favoured and therefore only a lower limit could be evaluated for the subsystem constants from the sensitivity limit of the NMR analysis:

$$(K_i)_P \text{ and } (K_i)_B < 5\times10^{-4}.$$

As previously noted, thermodynamic results[11] allow a more precise determination of the $(K_i)_B$: 1.2×10^{-4} ($i = 1$) and 1.4×10^{-11} ($i = 2$). Nevertheless the intersystem constant K_I can be estimated from the two samples (R = 1.16 and 1.35) mentioned in Table 2A.

$$K_I = 0.7\pm0.1 \text{ at } 120°\text{C} \quad \text{and} \quad Af_{Cl} = 0.9\pm0.4.$$

3. *The* $B(NEt_2)_3/OPCl_3$ *system (III)*

The equilibrium molar distribution have been obtained for 8 mixtures ($0.75 < R < 2.43$). The most significative data are reported in Table 2A. The behaviour of this system is very reminiscent of the previous two and leads to the following estimated constants:

$$(K_i)_P < 5\times10^{-4}$$
$$(K_1)_B = 1.2\times10^{-4}; \qquad (K_2)_B = 1.4\times10^{-11}$$
$$K_I = 0.1\pm0.1; \qquad Af_{Cl} = 0.9\pm0.3.$$

Table 2B. Equilibrium data in mol.% in system $B(NEt_2)_3$ vs BCl_3 at 25°C

$R = [Cl]/[B]$	C_r $B(NEt_2)_3$	$BCl(NEt_2)_2$	$BCl_2(NEt_2)$	BCl_3
0.73^a	24.2^b	75.8	—	—
0.84	11.5	88.5	—	—
1.15	—	79.1	20.9	—
1.62	—	40.1	59.9	—
2.04	—	—	90.8	9.2

(a), (b). See footnotes in Table 2A.

Although in the two last systems the need for complimentary data on the behaviour of the subsystems involving OP and SP moieties prevent us from getting accurate values of the disproportionation constants $(K_i)_P$, it is obvious that in the three systems under investigation these constants would be low ($\leq 5\times10^{-4}$). In other words the four subsystems LPX_3/LPY_3 (L = lone pair, O or S) and BX_3/BY_3 ($X = NEt_2$, $Y = Cl$) are characterized by a pronounced departure from ideal randomness, as was expected on the basis of previous work[10].

Nevertheless the data obtained in this study do not bear out a striking difference between the triply bonded phosphorus system and the corresponding ones where phosphorus is quadruply coordinated. However the redistribution rates seem to differ significantly. Thus, for example, a few hours at 25°C are sufficient to achieve complete redistribution on triply connected phosphorus while three weeks of heating at 120°C are necessary for quadruply connected phosphorus.

The intersystem and affinity constants are not much affected by the nature of the phosphorus moiety and have values not far from those calculated for random process. Minor differences which indicate slight but significative preference of attachment of substituents to specific central moieties must be noted. When K_I and Af_{Cl} is larger than 1.00 (system I) chlorine is preferentially associated with phosphorus. For values of K_I and Af_{Cl} smaller than 1.00 (systems II and III) the reverse situation is to be found. These data are in agreement with previous results[12–13] which lead to the conclusion that phosphorus moieties could be classified according to their relative affinity for chlorine vs NEt_2 ligands as in the following series:

$$\text{MeP} > \text{MeP(S)}, \text{MeP(O)}$$
$$[\text{MeP}, \text{MeP(S)}, \text{MeP(O)}/\text{Me}_2\text{Si}; \text{Cl/NMe}_2].$$

Moreover, in order to explain the behaviour of the two substituents ($X = NEt_2$, $Y = Cl$) in these systems, we can assume, for system (I), the more effective π donor ligand (NEt_2) would be bonded to the better acceptor $(-\mathrm{B}{<})$, while in systems (II) and (III) the presence of oxygen or sulphur bonded to a phosphorus center could enhance its effective electronegativity, possibly increasing its acceptor ability to such a degree that it becomes superior to the boron containing entities in this respect.

[†] According to these authors, the formation enthalpies of the mixed species are: −11.37 kcal for $BCl_2(NEt_2)$ and −7.83 kcal for $BCl(NEt_2)_2$.

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