EXCHANGE OF HALOGENS BETWEEN METHYLTRIIODOGERMANE AND METHYLPHOSPHONOTHIOIC DICHLORIDE

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Abstract – The equilibrium constants for the exchange of chlorine and iodine between the methylgermanium and the methylphosphorus moiety were measured using proton nuclear magnetic resonance spectroscopy. The value of the intersystem equilibrium constant shows that – in agreement with earlier predictions – at equilibrium chlorine is preferentially associated with the methylphosphorus moiety.

INTRODUCTION

IN AN earlier study of the exchange of halogens between methylgermanium and various methylphosphorus moieties, [1] sets of equilibrium constants governing the distribution of pairs of halogens between the two kinds of moieties were reported. Some of the data presented in that paper could be utilized to predict halogen-halogen exchange equilibria in systems which had not yet been studied experimentally. The present paper reports an investigation of the halogen-halogen exchange in the system CH_3GeI_3 vs. $CH_3P(S)Cl_2$, a system for which equilibrium constants were predicted on the basis of the data in the paper mentioned above and for which, however, experimental data were not available at that time.

EXPERIMENTAL

The preparation of the reagents as well as the experimental technique and procedure for obtaining the complete set of equilibrium constants were described previously[1]. Mixtures of CH_3GeI_3 and $CH_3P(S)Cl_2$ in benzene solution (1:5 by volume) reached equilibrium after at least 66 hr at 120° with the experimental data reported in Table 1 corresponding to a total reaction time of 8 days at this temperature. The rate of equilibration at room temperature was too slow for practical purposes.

Proton nuclear magnetic resonance (NMR) shifts of the methyl groups of the various molecular species present at equilibrium are listed below (in ppm relative to internal tetramethylsilane) with coupling constants (in c.p.s.) given in parenthesis: $CH_3P(S)I_2, -3\cdot193$ (12·4); $CH_3P(S)CII, -2\cdot607$ (12·9); $CH_3P(S)CI_2, -2\cdot148$ (13·9); $CH_3GeI_3, -2\cdot282$; $CH_3GeCI_2, -1\cdot803$; $CH_3GeCI_2I, -1\cdot388$; $CH_3GeCI_3, -1\cdot025$. These shifts were measured in a sample containing approximately equimolar amounts of both starting components.

RESULTS AND DISCUSSION

The experimental data shown in Table 1 clearly indicate that CH_3GeI_3 and $CH_3P(S)Cl_2$ at 120° exchange halogens quite readily resulting in a mixture of compounds having the general formulae $CH_3GeCl_nI_{3-n}$ and $CH_3P(S)Cl_mI_{2-m}$, where *n* ranges from 0 to 3 and *m* from 0 to 2. Following previous practice[1] a set of four equilibrium constants is chosen to describe all equilibria between the seven compounds of this system. This set represents one of the minimum number

^{1.} K. Moedritzer and J. R. Van Wazer, Rev. Chim. Minerale 6, 293 (1969).

R = [CI]/	$R' \equiv [Ge]/$							
[Ge+P]	[Ge+P]	CH ₃ P(S)I ₂	CH ₃ P(S)CII	CH ₃ P(S)Cl ₂	CH ₃ Gel ₃	CH ₃ GeCII ₂	CH ₃ GeCl ₂ I	CH _s GeCl _s
0-442*	*677-0	4.5†	L-L	2-6	58.5	15.9	3-0	0.7
(0.511)‡	(0·781)‡	(5-5)§	(8-0)	(8.6)	(61-2)	(14-5)	(2-0)	(0-2)
0.785	0-608	4.1	10-9	23-3	40-3	17-2	3.4	0-1
(0-845)	(0-619)	(5·5)	(12-5)	(21-2)	(41.5	(15-4)	(3-4)	(0-5)
1.233	0-384	3.5	14.4	41.6	21.2	13-1	5-0	1.1
(1·240)	(0-404)	(4·2)	(15-5)	(41-9)	(20-7)	(12-4)	(4-4)	(1-0)
1-474	0-263	2.8	14.7	54-4	12.2	9-2	4-9	1.9
(1-482)	(0-282)	(3.1)	(15-3)	(55·2)	(11-6)	(9·2)	(4-3)	([-3)
1.763	0.118	1.4	11-5	74-0	3.6	3.5	3.8	2.2
(1·772)	(0-131)	(1-5)	(12-3)	(74-4)	(3-0)	(4-0)	(3·2)	(1-6)
*From the †NMR dat	ingredients of that.	ne mixture.						

 \ddagger Calculated from the NMR data. §Calculated from the equilibrium constants K_1, K_2, K_3 , and K_1 for the R and R' values as obtained from the ingredients.

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Table 1. Experimental data and calculated values in the system CH₃GeI₃ vs. CH₃P(S)Cl₂ at equilibrium at 120°

sets of constants required to adequately describe all equilibria in mathematical terms.

The first constant considered here is the one governing the exchange of chlorines and iodines on the $CH_3P(S)$ moiety. This constant, the numerical value of which may be calculated readily [2, 3] from the data in Table 1, is shown below.

$$K_{1}^{120^{\circ}} = [CH_{3}P(S)Cl_{2}][CH_{3}P(S)I_{2}]/[CH_{3}P(S)ClI]^{2} = 0.74 \pm 0.12.$$
(1)

The value for $K_1^{120^\circ}$ of Equation (1), which has not been reported previously, is somewhat larger than the value expected for ideal randomness, $K_{\text{rand}} = 0.25$. Accordingly, the equilibrium concentration of the species $CH_3P(S)CII$ is less than expected for random distribution and the concentrations at equilibrium of the species $CH_3P(S)Cl_2$ and $CH_3P(S)I_2$ are larger than calculated for the random case.

Two additional constants represent the exchange of chlorine and iodine between the various species based on the methylgermanium moiety. These constants again were calculated from the experimental NMR data of Table 1 and are shown below.

$$K_{2^{33^{\circ}}} = [CH_{3}GeCl_{3}][CH_{3}GeCl_{2}]/[CH_{3}GeCl_{2}I]^{2} = 0.64 \pm 0.13$$
 (2)

$$K_{3}^{33^{\circ}} = [CH_{3}GeI_{3}][CH_{3}GeCI_{2}I]/[CH_{3}GeCII_{2}]^{2} = 0.59 \pm 0.09.$$
 (3)

Since exchange reactions on the methylgermanium moiety at room temperature are quite fast, the latter two equilibria correspond to the probe temperature of the NMR spectrometer which in this case was 33°. Again, the constants for the exchange of chlorine and iodine on the methylgermanium moiety are larger than the random value of $K_{rand} = 0.33$ and agree well with previously reported values $K_2 = 0.72 \pm 0.06$ and $K_3 = 0.79 \pm 0.07$ obtained in a study [4] of the equilibria in the system CH₃GeCl₃ vs. CH₃GeI₃. The observation that the equilibria for the chlorine-iodine exchange on a single central moiety deviate further from the random case than either the chlorine-bromine or bromine-iodine exchange is consistent with similar equilibrium data obtained in other systems [1]. In other words, this effect is real and probably is due to electronic effects within the molecule.

The fourth constant, the intersystem constant, deals with the distribution of chlorines and iodines between the germanium and phosphorus based moieties and may be expressed in the following form.

$$K_{I^{120^{\circ}}} = [CH_{3}GeCl_{3}]^{2}[CH_{3}P(S)I_{2}]^{3}/[CH_{3}GeI_{3}]^{2}[CH_{3}P(S)Cl_{2}]^{3} = (2\cdot3\pm0\cdot3)10^{-6}.$$
(4)

The value of K_{I} clearly shows that at equilibrium chlorine is preferentially associated with the phosphorus moiety. The equilibrium constant corresponds to the equilibrium at 120° since the transfer of chlorine and iodine between the two

^{2.} L. C. D. Groenweghe, J. R. Van Wazer and A. W. Dickinson, Analyt. Chem. 36, 303 (1964).

^{3.} A. R. Conrad and A. G. Lee, Analyt. Chem. 40, 659 (1968).

^{4.} K. Moedritzer and J. R. Van Wazer, Inorg. Chem. 5, 547 (1966).

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moieties at room temperature is quite slow so that rapid quenching of the samples held at 120° to the probe temperature of the NMR spectrometer preserves the equilibria at 120°.

The above constants K_1 , K_2 , K_3 and K_1 were then used to calculate [5] the theoretical mole percentage values (listed in parentheses in Table 1) of the various molecular species present at equilibrium for the over-all compositions characterized by the composition parameters R and R' shown in Table 1. Good agreement between experimental and theoretical values is observed in almost all cases.

The value of K_I in Equation (4) for the present system was predicted [1] earlier on the basis that the intersystem constant $(K_I)_E$ for the exchange of chlorine and bromine between $CH_3Ge \leftarrow$ and $CH_3P(S) \leftarrow$ as defined by

$$(K_{\rm I})_{\rm E} = [CH_3GeCl_3]^2 [CH_3P(S)Br_2]^3 / [CH_3GeBr_3]^2 [CH_3P(S)Cl_2]^3$$
(5)

and $(K_{I})_{F}$, the constant for the exchange of bromine and iodine between these moieties,

$$(K_{\rm I})_{\rm F} = [CH_3 GeBr_3]^2 [CH_3 P(S)I_2]^3 / [CH_3 GeI_3]^2 [CH_3 P(S)Br_2]^3$$
(6)

are interrelated by Equation (7).

$$K_{\rm I} = (K_{\rm I})_{\rm E} \cdot (K_{\rm I})_{\rm F}.$$
 (7)

Since the values reported for $(K_I)_E$ and $(K_I)_F$ correspond to 33° the value estimated for the intersystem constant for the exchange of chlorine and iodine between these two moieties, $K = 4 \times 10^{-8}$, also corresponds to this temperature. Using the integrated form of the van't Hoff equation the directly measured value of K_I in Equation (4) describing the equilibrium at 120° was converted to 33° resulting in $K_I^{33°} = 6.5 \times 10^{-8}$ which is quite close to the predicted value of 4×10^{-8} .

Comparing the intersystem constants for systems CH_3GeZ_3 vs. $CH_3P(S)T_2$, where Z and T are the exchangeable substituents, it appears that in each of the three cases, i.e., the pairs of exchangeable substituents Cl/Br, Br/I and Cl/I, the lighter halogen at equilibrium is preferentially associated with the methylphosphorus moiety. This tendency is greater for the Cl/I pair than for the Cl/Br pair is quite small for the Br/I pair.

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5. K. Moedritzer, L. C. D. Groenweghe and J. R. Van Wazer, J. phys. Chem. 72, 4380 (1968).

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