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THERMODYNAMIC FUNCTIONS OF GASEOUS BERYLLIUM, TITANIUM AND GERMANIUM ORGANOMETALLIC MOLECULES

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ABSTRACT

The thermal functions S_T^0, $-(G_T^0 - H_0^0)/T$ and $(H_T^0 - H_0^0)$ have been calculated from structural and spectroscopic data for the gaseous organometallics C_5H_5BeX (X = Cl, Br and BH_4), $C_5H_5MX_3$ (M = Ti and Ge; X = Cl, Br and I) and CH_3TiX_3 (X = Cl, Br and I). The rotational barriers of the C_5H_5 and CH_3 groups have been evaluated and discussed.

INTRODUCTION

The object of this work is to investigate the thermal properties of the gas phase of an interesting class of organometallic molecules of the kind C_5H_5BeX (X = Cl, Br, and BH_4), $C_5H_5MX_3$ and CH_3MX_3 (M = Ti and Ge, X = Cl, Br and I).

From a speculative point of view, it is interesting to evaluate the magnitude of rotational barriers and to correlate them to the type of ring–metal or methyl–metal bond involved. This information can be achieved from spectroscopic measurements of the torsional modes.

As is known, it is not easy to perform these experiments since torsional vibrations generally appear at low frequencies and their IR bands are weak. A further difficulty arises in the cases of low rotational barriers when the selection rules of the local symmetries often make torsional vibrations inactive.

The height of the internal rotation barrier is, however, evaluable from equations of statistical thermodynamics. It is also possible to check the accuracy of this determination if thermochemical data such as vapor pressure and heat capacity are available. In fact, the comparison between statistical and thermochemical $S_T^0(g)$ is a desirable test to check the correctness of barrier height determination.

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For a complete thermodynamic investigation of these compounds, enthalpy, entropy changes and a knowledge of the thermal functions of the solid and gas phases are required.

All the molecules investigated in this work, except C_5H_5BeCl and C_5H_5BeBr, exhibit internal rotation. This contribution cannot be completely neglected, even at moderate temperature, especially when low barriers hinder free rotation.

THERMODYNAMIC FUNCTIONS

The thermodynamic functions of a gaseous molecule are calculated as the sum of translational, rotational, vibrational and electronic contributions. Each contribution is evaluable from statistical thermodynamics in the rotator–harmonic oscillator approximation [1].

Translational and rotational contributions

In contrast to the degrees of internal freedom which require spectroscopic and structural data, translation is computable from the molecular weight. Bond lengths and angles are needed for the rotational contribution in order to calculate the principal moment of inertia. Structural information is available from electron diffraction and microwave studies for $C_5H_5TiCl_3$ [2], $C_5H_5TiBr_3$ [3], $C_5H_5BeBH_4$ [4], C_5H_5BeCl [5] and C_5H_5BeBr [6].

Since no report of microwave or electron diffraction studies has been cited for the remaining $C_5H_5GeX_3$, $C_5H_5TiI_3$ and CH_3TiX_3 molecules, some assumptions on the structural parameters were made.

(a) The molecular structures of the $C_5H_5MX_3$ systems were assumed to be the same as $C_5H_5TiCl_3$ [2] and $C_5H_5TiBr_3$ [3]. The CH_3TiX_3 molecules were considered structurally identical to CH_3GeCl_3 [7]. These assumptions are suggested by our IR and Raman spectra.

(b) The bond lengths and angles of $C_5H_5TiBr_3$ [3] were transferred to $C_5H_5TiI_3$.

(c) The C–C and C–H distances of the C_5H_5 ring were assumed equal to 1.42 Å and 1.10 Å, respectively, for all the cyclopentadienyls [8].

(d) The C_5H_5–Ge distance was calculated from the known C_5H_5–Ti bond [2], subtracting Ti and adding Ge atomic radii. The same procedure was followed to derive the CH_3–Ti distance starting from the known CH_3–Ge bond length [8] and from the Ge and Ti atomic radii.

(e) The geometrical data of the $GeCl_3$ and $GeBr_3$ groups were taken from CH_3GeCl_3 [9] and $Br_3GeMn(CO)_5$ [10], respectively. The Ge–I bond distance was estimated as the sum of the Ge and I atomic radii and the I–Ge–I angle was assumed to be the same as Br–Ge–Br [10].

(h) The structural data of the TiX_3 groups in the CH_3TiX_3 species were taken from the corresponding $C_5H_5TiX_3$ molecules.

TABLE 1

Geometrical data used to calculate the rotational contribution

	C_5H_5BeCl	C_5H_5BeBr	$C_5H_5BeBH_4$
C–C (Å)	1.424	1.424	1.422
C–H (Å)	1.097	1.088	1.117
Be–ring (Å)	1.484	1.528	1.485
Be–X (Å)	1.838	1.943	
Be–B (Å)			1.88
$Be–H_{(b)}$ (Å)			1.79
$B–H_{(b)}$ (Å)			1.29_5
$B–H_{(t)}$ (Å)			1.17
Be–B–H (deg)			65
$H_{(t)}$–B–H (deg)			124

	$C_5H_5TiCl_3$	$C_5H_5TiBr_3$	$C_5H_5TiI_3$
C–C (Å)	1.40	1.41	1.41
C–H (Å)	1.10	1.10	1.10
Ti–ring (Å)	2.06		
Ti–C (Å)		2.336	2.336
Ti–X (Å)	2.27	2.31	2.52
X–Ti–X (deg)	104	101	101
Cl–Ti–ring (deg)	113		

	$C_5H_5GeCl_3$	$C_5H_5GeBr_3$	$C_5H_5GeI_3$
C–C (Å)	1.41	1.41	1.41
C–H (Å)	1.10	1.10	1.10
Ge–ring (Å)	1.96	1.96	1.96
Ge–X (Å)	2.13_5	2.31	2.52
X–Ge–X (deg)	110.13	105	105

	CH_3TiCl_3	CH_3TiBr_3	CH_3TiI_3
Ti–X (Å)	2.27	2.31	2.52
$Ti–CH_3$ (Å)	2.04_5	2.04_5	2.04_5
C–H (Å)	1.083[a]	1.083[a]	1.083[a]
H–C–H (deg)	108[a]	108[a]	108[a]
X–Ti–X (deg)	104	101	101

[a] See ref. 19.

The geometrical parameters are summarized in Table 1.

We calculated that an uncertainty of ±0.25 Å on the bond distance and ±5° on the angle affects S_T^0 and $-(G_T^0 - H_0^0)/T$ by ±0.3 cal mole^{-1} K^{-1}.

TABLE 2

IR and Raman bands (cm^{-1}) and their assignment [a]

C_5H_5BeCl		C_5H_5BeBr		$C_5H_5BeBH_4$		Assignment
(IR, R)	(R)	(IR, R)	(R)	(IR, R)	(R)	C_{5v}
3125		3127		3126		A_1
1122		1124		1127		A_1
794		797		744		A_1
1257 [b]		1260 [b]		1254 [b]		A_2
3117		3120		3115		E_1
1431		1428		1434		E_1
1021		1024		1023		E_1
862		864		865		E_1
	3100		3103		3102	E_2
	1355		1351		1351	E_2
	1242		1245		1237	E_2
	1059		1062		1044	E_2
	850		850		847	E_2
	630		631		625	E_2
314		306				A_1
482		472				E_1
176		167				E_1
920		866				A_1
				2433		A_1
				2166		A_1
				1484		A_1
				1133		A_1
				900		A_1
				1179		A_2
				2485		B_1
				998		B_1
				182		B_1
				2177		B_2

1472	B_2
821	B_2
	C_s
392	A'
497	A'
473	A''
215	A'
220	A''
425	A'

$C_5H_5TiCl_3$		$C_5H_5TiBr_3$		$C_5H_5TiI_3$		$C_5H_5GeCl_3$		$C_5H_5GeBr_3$		$C_5H_5GeI_3$		Assignment
(IR, R)	(R)	(IR, R)	(R)	(IR, R)	(R)	(IR, R)	(R)	(IR, R)	(R)	(IR, R)	(R)	C_{5v}
3125		3125		3125		3130		3127		3125		A_1
1120		1118		1117		1122		1117		3125		A_1
838		835		837		822		820		818		A_1
1265 [b]		1265 [b]		1266 [b]		1270 [b]		1264 [b]		1260 [b]		A_2
3115		3109		3111		3120		3117		3115		E_1
1420		1425		1419		1428		1426		1424		E_1
1010		1019		1012		1020		1016		1012		E_1
822		817		815		811		820		808		E_1
	3108		3111		3114		3126		3120		3119	E_2
	1462		1465		1454		1450		1447		1444	E_2
	1241		1237		1227		1230		1228		1226	E_2
	1060		1055		1045		1080		1077		1069	E_2
	910		916		905		990		988		984	E_2
	490		497		485		518		516		513	E_2
												C_{3v}
465		425		426		437		401		380		A_1
444		285		231		427		318		251		E

TABLE 2 (continued)

$C_5H_5TiCl_3$		$C_5H_5TiBr_3$		$C_5H_5TiI_3$		$C_5H_5GeCl_3$		$C_5H_5GeBr_3$		$C_5H_5GeI_3$		Assignment
(IR, R)	(R)	(IR, R)	(R)	(IR, R)	(R)	(IR, R)	(R)	(IR, R)	(R)	(IR, R)	(R)	C_{5v}
337		209		197		405		235		195		A_1
298		300		300		290		201		108		E
199		152		126		184		152		141		E
182		123		110		150		131		70		E
143		88		67		139		119		96		A_1

CH_3TiCl_3 (IR, R)	CH_3TiBr_3 (IR, R)	CH_3TiI_3 (IR, R)	Assignment C_{3v}
2943	2935	2925	A_1
1259	1244	1238	A_1
652	619	605	A_1
393	305	210	A_1
148	125	98	A_1
3000	3008	3010	E
1418	1406	1400	E
823	820	816	E
451	351	268	E
189	168	153	E
152	107	71	E

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[a] Perkin-Elmer 180 B and Cary Raman 81 He–Ne Laser spectrometers used for IR and Raman measurements.

[b] From condensed phase as breakdown of C_{5v} selection rules.

Electronic contribution

The electronic states of a molecule are needed to perform the calculation of the electronic partition functions. However, this contribution is meaningful for high degeneracy levels and at temperatures for which the $\exp(-\epsilon/kT)$ value is not negligible. Generally, at moderate temperature there is no electronic contribution and the term which must be considered is $R \ln g$ where g is the $(2S+1)$ spin multiplicity of the ground state. No electronic levels are known for these organometallics; however, $(2S+1)$ can be assumed as a singlet. This statement appears acceptable in the light of possible ab initio spin configurations of these molecules.

Vibrational and internal rotation contributions

The calculation of the vibrational contribution is performable knowing the $3n-6$ normal modes and their vibrational symmetries. IR and Raman spectra provide this information, allow interesting structural considerations, and give indications on rotation barriers. Therefore these spectra were recorded and interpreted. The results of the vibrational investigation are reported in Table 2. This study was aided by the knowledge of previous IR and Raman data, mainly in solid and liquid phases and concerning C_5H_5GeCl [11], $C_5H_5BeBH_4$ [11], $Be(CH_3)_2$ [11], $C_5H_5TiCl_3$ [12] and metallocenes [13]. The assignment of the frequencies of C_5H_5BeCl and $C_5H_5BeBH_4$ was straightforward because their spectra have been previously interpreted [11]. The vibrational study of the spectra of the other molecules was performed on the basis of the usual assumptions of local symmetries [11,14]. Consequently, the vibrations of the C_5H_5 ring were treated under C_{5v} symmetry, those of the groups MX_3(M=Ti and Ge) and of CH_3 under C_{3v} symmetry and those of BH_4 under C_{2v} symmetry.

It was observed experimentally that the vibrations of these groups follow the selection rules of the highest local symmetry and this fact leads to the conclusion that low rotational barriers must be expected. According to the selection rules of the local symmetries, no torsional band can appear in the spectra because this A_2 mode is IR and Raman inactive both in the C_{3v} and C_{5v} symmetries. Our spectra do not show any band which can be assigned to the internal rotation frequency. $C_5H_5BeBH_4$ is the only molecule considered in this study for which these considerations are not strictly valid. In fact, some vibrations are at the same time IR and Raman active and, in particular, the A_2 inactive ring mode undergoes IR and Raman activation. This fact suggests the presence of a significantly higher barrier to which the measured 425 cm^{-1} band was associated by analogy with the 418 cm^{-1} Raman band observed in solid and liquid phases [11]. A barrier of 1.4 kcal $mole^{-1}$ is related to this frequency. The barrier height was calculated through the equation [15]

$$V = \frac{8\pi^2 c I_\mathrm{r} \bar{\nu}^2}{hn^2} \tag{1}$$

where $\bar{\nu}$ is the torsional frequency, n is the internal rotation number and I_r the reduced moment of inertia.

This direct evaluation could not be followed for the other molecules with internal rotation because the torsional frequencies are not experimentally observable.

In spite of this fact, statistical thermodynamics provides the equations to derive the barrier height indirectly. At temperature T, free internal rotation entropy is given by equation [16]

$$S^0_{\mathrm{f.i.r.}} = \frac{R}{2}\left[\ln T + \ln I_\mathrm{r} - 2\ln(n) + \ln\left(\frac{8\pi^3 k}{h^2}\right) + 1\right] \tag{2}$$

At the same temperature, $S^0_{\mathrm{f.i.r.}} = S^0_{\mathrm{vib}}$ and

$$S^0_{\mathrm{vib}} = -R\left\{\ln[1 - \exp(-u)] - \frac{u}{[\exp(u) - 1]}\right\} \tag{3}$$

TABLE 3

Calculated torsional parameters

	$C_5H_5BeBH_4$	$C_5H_5TiCl_3$	$C_5H_5TiBr_3$	$C_5H_5TiI_3$
I_r (g cm^2)	7.82×10^{-40}	1.47×10^{-38}	1.65×10^{-38}	1.56×10^{-38}
Q_f (cm^{-1})	$0.0781\ T^{1/2}$	$0.274\ T^{1/2}$	$0.307\ T^{1/2}$	$0.233\ T^{1/2}$
	425	88	82	84
V (cal mole^{-1})	1436	518	515	508

	$C_5H_5GeCl_3$	$C_5H_5GeBr_3$	$C_5H_5GeI_3$
I_r (g cm^2)	1.56×10^{-38}	1.72×10^{-38}	1.87×10^{-38}
Q_f (cm^{-1})	$0.307\ T^{1/2}$	$0.244\ T^{1/2}$	$0.255\ T^{1/2}$
	86	82	79
V (cal mole^{-1})	524	524	517

	CH_3TiCl_3	CH_3TiBr_3	CH_3TiI_3
I_r (g cm^2)	5.63×10^{-40}	5.65×10^{-40}	5.66×10^{-40}
Q_f (cm^{-1})	$0.0221\ T^{1/2}$	$0.0221\ T^{1/2}$	$0.0222\ T^{1/2}$
	90	90	90
V (cal mole^{-1})	518	523	520

TABLE 4

Thermodynamic functions of C_5H_5BeX, $C_5H_5MX_3$ and CH_3TiX_3 gaseous molecules [a]

T (K)	$-(G^0_T-H^0_0)/T$ (cal mole^{-1} K^{-1})	$(H^0_T-H^0_0)$ (cal mole^{-1})	S^0_T (cal mole^{-1} K^{-1})
C_5H_5BeCl			
298.15	60.2	4235	74.4
300	60.3	4260	74.5
350	62.6	5571	78.5
400	64.8	7044	82.4
450	67.0	8683	86.3
500	69.1	10468	90.0
550	71.2	12386	93.7
600	73.2	14420	97.2
	±0.5	±30	±0.5
C_5H_5BeBr			
298.15	60.5	4274	74.8
300	60.5	4319	74.9
350	62.9	5617	78.9
400	65.1	7094	82.9
450	67.3	8737	86.7
500	69.5	10528	90.5
550	71.5	12450	94.2
600	73.6	14487	97.7
	±0.5	±30	±0.5
$C_5H_5BeBH_4$			
298.15	62.8	4844	79.9
300	62.9	4895	79.2
350	65.6	6457	84.0
400	67.8	8266	88.5
450	70.8	10272	93.6
500	73.1	12476	98.1
550	75.6	14857	102.6
600	78.0	17398	107.0
	±0.5	±30	±0.5
$C_5H_5TiCl_3$			
298.15	70.3	5426	88.5
300	70.4	5460	88.6
350	73.3	6790	92.7
400	76.0	8120	96.3
450	78.4	9540	99.6
500	80.7	11020	102.7
550	82.8	12559	105.6
600	84.8	14120	108.3
	±0.5	±30	±0.5
$C_5H_5GeCl_3$			
298.15	76.5	6470	98.2
300	76.5	6570	98.4
350	80.1	8400	104.1

TABLE 4 (continued)

T (K)	$-(G^0_T-H^0_0)/T$ (cal mole^{-1} K^{-1})	$(H^0_T-H^0_0)$ (cal mole^{-1})	S^0_T (cal mole^{-1} K^{-1})
400	83.4	10480	109.6
450	86.7	12555	114.6
500	89.7	14950	119.6
550	92.7	17380	124.3
600	95.4	19980	128.7
	±0.8	±50	±0.8
$C_5H_5GeBr_3$			
298.15	82.8	7061	106.5
300	82.9	7140	106.7
350	86.8	9027	112.6
400	90.3	11134	118.8
450	93.7	13363	123.4
500	96.9	15743	128.4
550	100.0	18232	133.1
600	103.0	20806	137.7
	±0.8	±50	±0.8
$C_5H_5TiBr_3$			
298.15	82.2	7117	106.1
300	82.3	7194	106.3
350	86.2	9121	112.3
400	89.8	11200	117.8
450	93.2	13455	123.1
500	96.4	15870	128.1
550	99.5	18389	132.9
600	102.5	21020	137.5
	±0.5	±30	±0.5
$C_5H_5TiI_3$			
298.15	86.0	7364	110.7
300	86.1	7440	110.9
350	90.1	9380	116.9
400	93.8	11480	122.5
450	97.3	13725	127.8
500	100.6	16100	132.8
550	103.7	18645	137.6
600	106.7	21276	142.2
	±0.8	±50	±0.8
$C_5H_5GeI_3$			
298.15	90.0	7633	115.6
300	90.3	7650	115.8
350	94.2	9695	121.9
400	98.1	11720	127.4
450	101.6	13995	132.7
500	105.0	16450	137.9
550	108.1	18975	142.6
600	111.3	21480	147.1
	±0.8	±50	±0.8

TABLE 4 (continued)

T (K)	$-(G^0_T\text{-}H^0_0)/T$ (cal mole^{-1} K^{-1})	$(H^0_T\text{-}H^0_0)$ (cal mole^{-1})	S^0_T (cal mole^{-1} K^{-1})
CH_3TiCl_3			
298.15	70.3	5426	88.5
300	70.4	5460	88.6
350	73.3	6790	92.7
400	76.0	8120	96.3
450	78.4	9540	99.6
500	80.7	11020	102.7
550	82.8	12559	105.5
600	84.8	14120	108.3
	±0.8	±50	±0.8
CH_3TiBr_3			
298.15	75.7	5784	95.1
300	75.8	5820	95.2
350	78.9	7175	99.4
400	81.7	8560	103.1
450	84.3	9990	106.5
500	86.6	11550	109.7
600	90.9	14640	115.3
	±0.8	±50	±0.8
CH_3TiI_3			
298.15	82.0	6142	102.6
300	82.1	6180	102.7
350	85.3	7560	106.9
400	88.3	8960	110.7
450	91.0	10440	114.2
500	93.4	12000	117.4
550	95.7	13530	120.3
600	97.9	15120	123.1
	±0.8	±50	±0.8

[a] A Univac 1100/82 computer was used for the calculations.

with u equal to $1.4388\ \bar{\nu}/T$.

The torsional frequency, $\bar{\nu}$, can then be obtained by combining eqns. (2) and (3). Thus the rotational barrier, V, related to the $\bar{\nu}$ frequency is computable from eqn. (1). These barriers are summarized in Table 3 together with the torsional constants.

We have previously underlined that the knowledge of rotation barriers is important for the correct evaluation of thermal functions. As theorized by Pitzer [17,18], the presence of rotational barriers requires corrections to the thermal functions based on $1/Q_f$ and V/RT values where Q_f is the partition function for free internal rotation and V is the barrier height. These corrections were performed by linear interpolation of the $1/Q_f$ and V/RT values using Pitzer's tables [17,18]. In Table 3, the values of Q_f and V used in these computations are reported.

Finally, the values of each contribution at the same temperature are added to give the final entropy, free-energy and heat content values.

The thermal functions of the studied organometallic molecules are reported in Table 4. The uncertainties associated to each quantity were computed on the basis of possible error sources in the experimental and estimated geometrical factors and in the spectroscopic measurements.

CONCLUSIONS

The analysis of the rotational barriers determined for the three classes of molecules suggests some considerations on the factors contributing to their magnitudes. The 0.5 cal mole^{-1} barriers of $C_5H_5TiX_3$ and $C_5H_5GeX_3$ can arise from two distinct factors. The first contribution is related to the steric effect between the halides and the ring and the second is due to the overlap of the appropriate symmetry orbitals $\pi(a_1, e_1, e_2)$ of C_5H_5 and $\{d(a_1, e_1, e_2), s(a_1)$ and $p(a_1, e_1)\}$ of the transition metal.

The latter, although theoretically possible, ought to be regarded as uninfluential when we consider the CH_3TiX_3 molecules. It is evident, in fact, that the methyl group is bonded to titanium via a σ bond and no π orbitals are involved; however, both the cyclopentadienyls and the methyl trihalides present the same barriers.

We believe that the significantly high barrier in $C_5H_5BeBH_4$ can be explained by a consistent overlap between the $2p$ and the π orbitals of beryllium and the five-membered ring, respectively. This approach is supported by the 1.48 Å C_5H_5–Be distance [5] which is significantly shorter than the corresponding 2.06 Å of the C_5H_5–Ti bond [3].

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