Bis(methylcyclopentadienyl) Derivatives of Germanium(II), Tin(II), and Lead(II): ¹H and ¹³C NMR Properties and Comparison with Those for Analogues Formed by Univalent Metals (Li, K, and Tl)

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Bis(methylcyclopentadienyl)germanium(II) has been isolated and found to be moderately stable toward polymerization. Comparison of ¹H and ¹³C NMR parameters with those for homoleptic tin and lead compounds indicates that in solution all three adopt a skew sandwich structure, first confirmed for $Pb(C_5H_5)_2$ by vapor-phase electron diffraction. Carbon-13 chemical shifts for lithium, potassium, and thallium(I) derivatives of methylcyclopentadiene have been measured and relationships with those for the group 4 compounds are discussed in terms of bonding and electronegativity effects. In all cases a marked low-field displacement away from corresponding shifts for transition-metal π complexes has been found. The tin-119 NMR spectrum of $Sn(C_5H_4CH_3)_2$ measured by the ¹H{¹¹⁹Sn} INDOR technique consists of a nonet, confirming equivalence at $-40\ ^\circ C$ between the two methylcyclopentadienyl rings, centered at more than 2100 ppm upfield from ¹¹⁹Sn shifts for Sn(IV) analogues.

Introduction

The synthesis of bis(methylcyclopentadienyl)tin was first reported in 1959 by Wilkinson and co-workers,[1] following a route analogous to that used somewhat earlier by Fischer and Grubert[2] to obtain bis(cyclopentadienyl)tin. Together these two unusual compounds have enjoyed a unique position as the single instance of thermally stable bivalent derivatives in the otherwise very extensive organometallic chemistry of tin. A change in this situation came about only recently[3] when, using sterically restrictive alkyl groups such as bis(trimethyl-silyl)methyl, Davidson and Lappert[4] were able to isolate several further diorganotin(II) species. Despite this development, the structural chemistry of the cyclopentadiene compounds has remained a peculiarity of substantial interest. On the basis of IR and dipole measurements, Wilkinson first proposed[1] the angular "sandwich" structure (I) subsequently substantiated

I
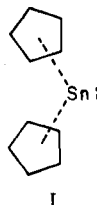
for $Sn(C_5H_5)_2$ in the gas phase using electron diffraction.[5] An analogous structure has been suggested for $Sn(C_5H_4CH_3)_2$, on the basis of vibrational spectroscopy;[6] a recent investigation of $Sn(C_5H_5)Cl$ by x-ray methods located[7] the metal atom perpendicular to the cyclopentadienyl ring, though somewhat distorted from C_5 symmetry.

The structure of solid bis(cyclopentadienyl)lead(II)[8] has been determined using x-ray crystallography.[9] In this compound adjacent metal atoms are held together by bridging C_5H_5 units oriented at right angles to the chains thus formed; the coordination of each lead atom is completed by interaction with a nonbridging C_5H_5 group. The preparation of $Pb(C_5H_4CH_3)_2$ has also been documented[1] but its properties have not been investigated further.

The bivalent state is not well established for germanium,[10] and bis(cyclopentadienyl)germanium(II) was first reported only recently.[11] This compound was said to be monomeric in benzene solution but polymerization to insoluble material was rapid (3 h) at ambient temperature, possibly with the formation of Ge-Ge bonds. We have succeeded in isolating a methylcyclopentadienyl analogue, a yellow liquid compound

which appears when pure to be more resistant to polymer formation.

Metallotropic character of quadrivalent group 4 compounds possessing cyclopentadienyl substituents has been recognized and subjected to detailed study using variable-temperature NMR spectroscopy.[12-14] However, the relationship of this type of behavior to the situation prevailing for $Sn(C_5H_5)_2$ and $Sn(C_5H_4CH_3)_2$ has not been established, since NMR properties of these latter systems have been only cursorily examined.[1,6] In this paper we present the results of a complete investigation by ¹H and ¹³C NMR spectroscopy of the compounds $M(C_5H_4CH_3)_2$, a homoleptic series of organometallic derivatives of bivalent germanium, tin, and lead. This series was chosen for study rather than the unsubstituted cyclopentadiene analogues not only in view of the enhanced stability of the germanium species but more significantly because of the effect of the asymmetry introduced by the methyl group. This results in ring nuclei becoming distinguishable by NMR experiments, the basis for our interest in nondegenerate metallotropism shown by (methylcyclopentadienyl)silanes, -germanes, and -stannanes.[14] For comparative purposes we have obtained ¹³C NMR data for three related derivatives of univalent metals, those of Li, K, and Tl(I), which are purported to possess varying degrees of ionicity.[15,16] Measurement of the ¹¹⁹Sn NMR spectrum of $Sn(C_5H_4CH_3)_2$ by ¹H{¹¹⁹Sn} heteronuclear magnetic double resonance also revealed a very pronounced upfield ¹¹⁹Sn chemical shift between this compound and a tin(IV) relative.[17]

Experimental Section

All manipulations were conducted under an atmosphere of dry dinitrogen gas. Methylcyclopentadiene was obtained by thermal "cracking" of the dimer followed by redistillation, bp 73 °C.[18] Solvents for the NMR studies were rigorously dried and degassed using standard procedures. Perkin-Elmer R12 or R32 spectrometers were used for the ¹H NMR measurements; ¹³C NMR data were collected at 15.1 MHz with proton noise decoupling using a Nicolet TT-14 Fourier transform spectrometer. The ¹H{¹¹⁹Sn} INDOR spectrum was obtained at -40 °C using the experimental arrangement described previously by Goodfellow et al.,[19] operating with a decoupling frequency of ca. 37.3 MHz for ¹¹⁹Sn.

Synthesis of Bis(methylcyclopentadienyl)germanium(II). In a typical reaction, potassium methylcyclopentadienide (10 mmol) was synthesized in an evacuated double-limbed Schlenk apparatus[20] from the metal (0.40 g) and excess methylcyclopentadiene monomer in dry diethyl ether and was freed from volatile material by evacuation (10^{-3} mmHg) at 60 °C over 24 h. After addition of GeI_2 (1.5 g, 4.60 mmol), dry benzene (25 cm³) was condensed in and the reaction mixture was

Table I. Proton Chemical Shifts[a] for $M(C_5H_4CH_3)_2$, M = Ge, Sn, or Pb, at 308 K

Compd	$\delta(H_{av(Cp)})$	$\delta(H_{Me})$	Solvent
$Ge(C_5H_4CH_3)_2$	5.72	2.08	$CDCl_3$
$Sn(C_5H_4CH_3)_2$	5.65	1.99	$CDCl_3$
$Pb(C_5H_4CH_3)_2$	5.39	2.78	C_6D_6

[a] Measured at 60.0 and 90.0 MHz, downfield positive from internal Me_4Si.

stirred at 10 °C for 3 h. This was followed by removal of the benzene, addition of dry pentane (20 cm³), and repeated extraction through the central frit by back-and-forth condensation until the extract became colorless. After the pentane was pumped away, a clear, light yellow oil remained, identified by infrared, NMR, and mass spectroscopy as $Ge(C_5H_4CH_3)_2$. Anal. Calcd for $C_{12}H_{14}Ge$: C, 62.45; H, 6.07. Found: C, 61.92; H, 5.92. This compound was further characterized by its chemical reactivity as described below.

Synthesis of Other Methylcyclopentadienyl Compounds. Bis-(methylcyclopentadienyl)tin(II) was isolated as a pale yellow liquid through reaction of anhydrous tin(II) chloride and potassium methylcyclopentadienide in dry tetrahydrofuran as described by Wilkinson et al.[1] After redistillation, the product was characterized by IR[6] and ¹H NMR[1,6] measurements as well as by elemental analysis. Anal. Calcd for $C_{12}H_{14}Sn$: C, 52.00; H, 5.06. Found: C, 51.78; H, 4.97. Bis(methylcyclopentadienyl)lead(II) was prepared similarly from lead(II) acetate using monoglyme as solvent. The pale yellow, low-melting solid product[1] was extracted into benzene solution. Direct reaction in monoglyme between the alkali metal and methylcyclopentadiene was used to obtain the lithium and potassium salts; the thallium(I) derivative was prepared from thallium(I) sulfate in a basic aqueous medium in a manner identical with that previously described elsewhere for the corresponding cyclopentadiene compound.[16]

Results and Discussion

Upon stirring of a slurry of potassium methylcyclopentadienide and germanium(II) iodide in dry benzene,[21] the yellow color imparted by the latter became gradually less intense. After 3 h, recovery of pentane-soluble material afforded a very air-sensitive, light yellow oil, the infrared spectrum of which closely resembled that[6] of $Sn(C_5H_4CH_3)_2$. Its identity as bis(methylcyclopentadienyl)germanium(II) was established mass spectroscopically: the spectrum was dominated by ions with m/e 149–155, attributable to the loss of one ring to give $^nGe(C_5H_4CH_3)^+$, (n = 70–76) with a very weak series at m/e 228–234 corresponding to a molecular ion family and no fragments at higher mass values. These data parallel exactly those described earlier[6] for the tin(II) compound. Typical yields were in the range 55–70%, and additional characterization was provided by using ¹H and ¹³C NMR spectroscopy as discussed below as well as by studying the chemical behavior of the product. Thus with methyl iodide oxidative addition occurred to give a germanium(IV) derivative, $Ge(C_5H_4CH_3)_2(CH_3)(I)$; reaction with acetylacetone resulted in protolytic fracture of both Ge–ring linkages to give the known[22] $Ge(Acac)_2$. Further details of these and other aspects of the chemistry of $Ge(C_5H_4CH_3)_2$ will be presented shortly.[23]

Proton NMR data for the three bivalent group 4 derivatives are listed in Table I. The relatively large number of parameters observed for $Sn(C_5H_4CH_3)_2$ as a result of spin coupling with magnetic metal nuclei are collected in Table II. For the tin compound, the ¹H spectrum is deceptively simple as originally reported,[1] consisting only of two singlets in a 4:3 ratio.[24] Contrary to a subsequent statement,[6] no multiplicity of the low-field resonance could be detected down to –60 °C, although sought using a number of different samples and a variety of instrumentation.[25] At –40 °C satellite lines were present around the olefinic signal, due to coupling with ¹¹⁷Sn and ¹¹⁹Sn nuclei (abundances, respectively, 7.67, 8.68%) with ^2J = 17.0 Hz [Table II: cf.[1] 15.9 Hz for $Sn(C_5H_5)_2$]. These collapsed on raising the temperature, consistent with the onset

Table II. NMR Parameters[a] for Bis(methylcyclopentadienyl)tin

	Temp, K	$\delta(H_{av(Cp)})$	$\delta(H_{Me})$	$^2J(^1H_{av(Cp)}-^{117,119}Sn)$
¹H	308	5.65	1.99	Not obsd
	Ambient[b]	5.70	2.03	~10
	233	5.63	1.98	17.0[c]

	Temp, K	Posn[d]	δ	$J(^{13}C-^{117,119}Sn)^c$
¹³C	300	C_{Me}	16.76	
		C_1	126.70	
		$C_{2,5}$	113.80[e]	
		$C_{3,4}$	111.20[e]	
	218	C_{Me}	13.88	13.3
		C_1	123.50	11.8
		$C_{2,5}$	110.68	15.9
		$C_{3,4}$	108.37	12.8

	Temp, K	$\delta(^{119}Sn)$	$^2J(^1H_{av(Cp)}-^{117,119}Sn)$
¹H{¹¹⁹Sn}	233	-2171.1^f	17.0

[a] Coupling constants, Hz; chemical shifts, ppm measured positive downfield from Me_4Si (¹H or ¹³C) or negative upfield from $SnMe_4$ (¹¹⁹Sn). Samples ca. 50% v/v in dry $CDCl_3$. [b] Reference 6. [c] ¹¹⁷Sn and ¹¹⁹Sn components not fully resolved. [d] Posn is the carbon position in the methylcyclopentadienyl group, numbered by analogy with ring hydrogen positions (see text). [e] For discussion of assignment, see text. [f] Cf. Figure 2. Temperature effect ca. +0.3 ppm/°C increase.

Table III. ¹³C Chemical Shifts[a] for Methylcyclopentadienyl Derivatives at 300 K

Compd	$\delta(C_1)^b$	$\delta(C_{2,5})^b$	$\delta(C_{3,4})^b$	$\delta(C_{Me})$	Solvent
$Ge(C_5H_4CH_3)_2$	126.2	113.0	110.5	14.1	$CDCl_3$
$Sn(C_5H_4CH_3)_2$	123.6	110.8	108.5	14.0	$CDCl_3$
$Pb(C_5H_4CH_3)_2$	114.3	104.7	103.7	14.6	C_6H_6
$Li(C_5H_4CH_3)$	113.1	103.1	101.7	14.4	Monoglyme
$K(C_5H_4CH_3)$	113.4	104.0	102.9	14.7	Monoglyme
$Tl(C_5H_4CH_3)$	c	107.5	105.0	c	Monoglyme

[a] Downfield from Me_4Si = 0 ppm. [b] For discussion of numbering and assignment, see text. [c] Not observed due to low solubility of Tl(I) derivative.

of an intermolecular exchange process.[26] Similar coupling with the upfield (CH_3) resonance was not observed. Proton spectra for the germanium and lead analogues matched the 4:3 pattern for the tin compound exactly, with only minor chemical shift differences constituting an upfield trend in the olefinic resonant frequency with decreasing metal electronegativity.

Carbon-13 results are summarized in Table III and include those measured for the lithium, potassium, and thallium(I) derivatives of methylcyclopentadiene. The gross appearance of the spectra is exemplified by that at 27 °C for $Sn(C_5H_4CH_3)_2$, shown in Figure 1. Here the high-field resonance (16.76 ppm) is due to the methyl carbon atoms, while the three signals in the low-field region can be attributed to the C_5 ring carbon atoms, all with definite olefinic character. That with the largest downfield shift (126.7 ppm) shows significantly less Overhauser enhancement than the other two, identifying it as the C_1 atom, that bearing the methyl group in an averaged arrangement (II). The assignment given in Tables II and III

II
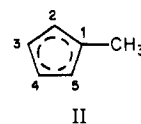
for the other two signals ($C_{2,5}$ and $C_{3,4}$, respectively) seems the more likely in relation to the influence of C_1 and the methyl group but is not unequivocal and could be reversed. On lowering the temperature to –55 °C, the only change was the appearance of spin coupling of all carbon atoms with the magnetically active tin isotopes (J in the range 11.8–15.9 Hz),
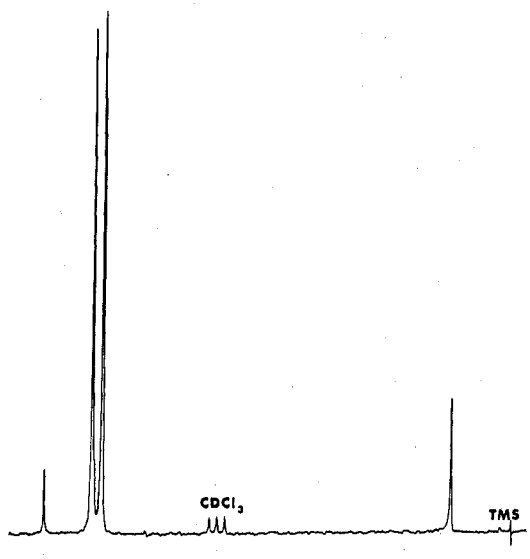
Figure 1. ^{13}C NMR spectrum of bis(methylcyclopentadienyl)tin(II) (^1H noise decoupled, 300 K); for chemical shifts vs. internal Me₄Si, see Table II.

Figure 2. $^1H\{^{119}Sn\}$ INDOR spectrum of bis(methylcyclopentadienyl)tin(II) at 233 K.

again consistent with a dissociative process operating at higher temperatures. For the germanium analogue the positions of resonances constituting the ab₂c₂x pattern were displaced only slightly to low field (Table III), while a more substantial upfield shift was evident in the case of the lead compound giving frequencies very close to those for the alkali-metal derivatives.

An attempt by Sergeyev[27] to classify metal cyclopentadienyl derivatives as σ (η^1) or π complexes (η^5) on the basis of ^{13}C chemical shifts and of $^1J(^{13}C-H)$ has recently been discounted by Fischer et al.[28] However, the close relationship between NMR parameters for $M(C_5H_4CH_3)_2$ (M = Ge, Sn, Pb) strongly suggests that in solution they share structure I, and it is likewise clear that for these compounds the ^{13}C shifts lie to low field of those in ionic[28] species typified by the potassium salt, although this effect is marginal for the lead derivative. The diamagnetic shift in ring-carbon resonances between M = Ge and Pb implies enhanced shielding associated with greater electron density on the ring, resulting from increased electropositive character of the metal atom. This in turn suggests greater charge separation in $Pb(C_5H_4CH_3)_2$ which may be correlated with the polymeric structure of solid bis-(cyclopentadienyl)lead.[9] Correspondingly, and in agreement with results for cyclopentadienyl analogues,[28] a modest paramagnetic effect occurs between $M(C_5H_4CH_3)$ (M = Li, K) and the thallium(I) derivative consistent with some degree of covalent character for the latter.[16] The significantly higher field shifts (70–93 ppm) found in transition-metal π-cyclopentadienyl complexes[27,28] may thus constitute an anomaly which parallels the behavior of ^1H or ^{19}F nuclei when bound to metal atoms with partly filled d levels[29] and carry no specific structural implication.

For $Sn(C_5H_4CH_3)_2$, the ^{119}Sn NMR spectrum was also measured, using the heteronuclear magnetic double-resonance technique. Very few chemical shifts for Sn(II) compounds have been recorded[30] and none is directly comparable with that for a covalent organometallic derivative. The ^{119}Sn shift of 2171.1 ppm *upfield* from tetramethyltin (Table II) contrasts with that for $Sn(C_5H_5)_4$: −27.2 ppm measured during this work, −25.9 ppm elsewhere.[31] This corresponds to a large increase in shielding for the tin(II) compound which is in the same sense as the change in Mössbauer isomer shift[6,26] and is directly attributable to substantially increased s-electron density at the tin atom. The nonet structure of the ^{119}Sn resonance, shown in Figure 2, agrees well with that predicted
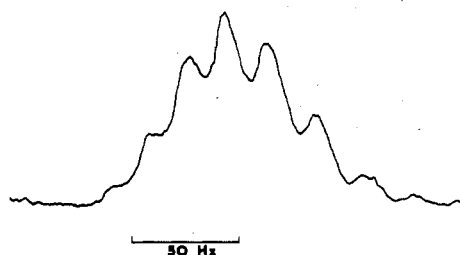
for coupling with eight equivalent nuclei with $I = {}^1/_2$. This is consistent with a set of near-equal ^2J values between the metal nucleus and the eight olefinic ring protons, despite the magnetic nonequivalence of the latter.

The bonding in the cyclopentadienyltin(II) derivatives has been rationalized[1,6] in terms of overlap of the a₁ ring π orbital with a metal orbital of the same symmetry derived from atomic 6s and 6p orbitals. This interaction has become referred to as "pseudo-π" bonding,[3,6,7] inviting comparison with ferrocene and related π-cyclopentadienyls.[1,3,6,7] It is interesting, therefore, that as stated above, the ^{13}C chemical shifts reported here lie well removed to low field from ^{13}C resonances of such metal π complexes and very close to those for tin(IV) analogues like $(CH_3)_3Sn(C_5H_5)$.[32] It is also noteworthy, though not commented on previously, that the geometry of the C₅H₅ unit in $Sn(C_5H_5)Cl$ is irregular in a manner which suggests uneven distribution of π-electron density around the ring.[7] Results of the present study offer no additional distinction for $Sn(C_5H_4CH_3)_2$ between the rapid metallotropism exhibited by tin(IV) cyclopentadienyls and the bonding requirements of the skew sandwich structure (I) but substantiate that the latter is common in solution to the three homoleptic group 4 species.

Registry No. Ge(C₅H₄CH₃)₂, 65495-43-4; Sn(C₅H₄CH₃)₂, 41430-03-9; Pb(C₅H₄CH₃)₂, 42186-69-6; Li(C₅H₄CH₃), 25586-80-5; K(C₅H₄CH₃), 41066-45-9; Tl(C₅H₄CH₃), 34034-67-8.

References and Notes

(1) L. D. Dave, D. F. Evans, and G. Wilkinson, *J. Chem. Soc.*, 3684 (1959).
(2) E. O. Fischer and H. Grubert, *Z. Naturforsch., B*, **11**, 423 (1956).
(3) A rather different kind of complex, involving interaction between, bivalent tin and a neutral benzene molecule, had also been reported by Amma and co-workers: H. Luth and E. L. Amma, *J. Am. Chem. Soc.*, **91**, 7515 (1969); M. S. Weininger, P. F. Rodesiler, A. G. Gash, and E. L. Amma, *ibid.*, **94**, 2135 (1972); P. F. Rodesiler, T. Auel, and E. L. Amma, *ibid.*, **97**, 7405 (1975).
(4) P. J. Davidson and M. F. Lappert, *J. Chem. Soc., Chem. Commun.*, 317 (1973).
(5) A. Almenningen, A. Haaland, and T. Motzfeldt, *J. Organomet. Chem.*, **7**, 97 (1967).
(6) P. G. Harrison and M. A. Healy, *J. Organomet. Chem.*, **51**, 153 (1973).
(7) K. Bos, E. J. Bulten, J. G. Noltes, and A. L. Spek, *J. Organomet. Chem.*, **99**, 71 (1975).
(8) E. O. Fischer and H. Grubert, *Z. Anorg. Allg. Chem.*, **286**, 237 (1956).
(9) C. Panattoni, G. Bombieri, and U. Cruatto, *Acta Crystallogr.*, **21**, 823 (1966), where the existence of a second polymorph of undetermined structure was also reported.
(10) F. Glockling, "The Chemistry of Germanium", Academic Press, New York, N.Y., 1969.
(11) J. V. Scibelli and M. D. Curtis, *J. Am. Chem. Soc.*, **95**, 924 (1973).
(12) A. Davison and P. E. Rakita, *J. Am. Chem. Soc.*, **90**, 4479 (1968); A. Davison and P. E. Rakita, *Inorg. Chem.*, **9**, 289 (1970); R. B. Larrabee, *J. Organomet. Chem.*, **74**, 313 (1974).
(13) P. C. Angus and S. R. Stobart, *J. Chem. Soc., Dalton Trans.*, 2374 (1973).
(14) A. Bonny, S. R. Stobart, and P. C. Angus, *J. Chem. Soc., Dalton Trans.* in press.
(15) J. M. Birmingham, *Adv. Organomet. Chem.*, **2**, 365 (1964).
(16) F. A. Cotton and L. T. Reynolds, *J. Am. Chem. Soc.*, **80**, 269 (1958).
(17) R. J. Goodfellow and S. R. Stobart, *J. Magn. Reson.*, **27**, 143 (1977).

(18) L. T. Reynolds and G. Wilkinson, *J. Inorg. Nucl. Chem.*, 9, 86 (1959).
(19) P. L. Goggin, R. J. Goodfellow, J. R. Knight, M. G. Norton, and B. F. Taylor, *J. Chem. Soc., Dalton Trans.*, 2220 (1973).
(20) This type of equipment is described in D. F. Shriver, "The Manipulation of Air-Sensitive Compounds", McGraw-Hill, New York, N.Y., 1969.
(21) L. S. Foster, *Inorg. Synth.*, 3, 63 (1950).
(22) A. Rogers and S. R. Stobart, *J. Chem., Soc., Chem. Commun.*, 52 (1976).
(23) A. D. McMaster and S. R. Stobart, unpublished results.
(24) Incorrectly reported as a 5:3 ratio in ref 1.
(25) We are unable to account for the appearance of the ^{1}H NMR spectrum for $Sn(C_5H_4CH_3)_2$ reproduced in ref 6, where $^2J(Sn-H)$ was also incorrectly given as ~10 Hz.

(26) P. G. Harrison and J. J. Zuckerman, *J. Am. Chem. Soc.*, 92, 2577 (1970).
(27) N. M. Sergeyev, *Prog. Nucl. Magn. Reson. Spectrosc.*, 9, 98 (1973).
(28) P. Fischer, J. Stadelhofer, and J. Weidlein, *J. Organomet. Chem.*, 116, 65 (1976).
(29) M. A. Cairns, K. R. Dixon, and J. J. McFarland, *J. Chem. Soc., Dalton Trans.*, 1159 (1975).
(30) P. J. Smith and L. Smith, *Inorg. Chim. Acta, Rev.*, 7 11 (1973).
(31) A. P. Tupciauskas, N. M. Sergeyev, and Yu. A. Ustynyuk, *Mol. Phys.*, 21, 179 (1971).
(32) Yu. K. Grishin, N. M. Sergeyev, and Yu. A. Ustynyuk, *J. Organomet. Chem.*, 22, 361 (1970); Yu. K. Grishin, N. M. Sergeyev, and Yu. A. Ustynyuk, *Org. Magn. Reson.*, 4, 377 (1972).

Mass Spectrometric Study of the Vapor-Phase Species of Brominated Polymeric Sulfur Nitride and Tetrasulfur Tetranitride

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The gas-phase species volatilized from $(SN)_x$ treated with bromine and tetrasulfur tetranitride (S_4N_4) treated with Br_2 and ICl were studied using mass spectrometric techniques. Conventional electron impact, chemical ionization, modulated molecular beam, and phase-angle mass spectrometry techniques were used to identify the gas-phase species. The species volatilized from brominated $(SN)_x$ and brominated S_4N_4 were identical, consisting of Br_2, NSBr, $(SN)_4$ isomers, and smaller amounts of HBr, S_2Br_2, and other sulfur-nitrogen compounds. The gas-phase species observed over S_4N_4 treated with ICl were I_2, ICl, S_4N_4, NSCl, HCl, HI, and small amounts of S_2Cl_2 and other sulfur-nitrogen compounds; Cl_2 and NSI were not observed. The vapors of S_4N_4 brominated in CS_2 solution were examined and found to yield HSCN, BrSCN, and CS_3N_2 species, in addition to HBr, NSBr, Br_2, and sulfur-nitrogen compounds. The gas-phase products formed on exposure of brominated samples to air were also studied.

Introduction

It has recently been reported that the addition of bromine to polymeric sulfur nitride, $(SN)_x$, results in the formation of blue-black brominated $(SN)_x$ crystals.[1-3] On exposure to Br_2 vapor, the $(SN)_x$ crystals swell in directions perpendicular to the $(SN)_x$ chains and form fibrous crystals of composition $(SNBr_{0.5})_x$.[1,3] By evacuation at 10^{-5} Torr for 1 h, a small amount of bromine is removed, resulting in a final composition of $(SNBr_{0.4})_x$.[3] It has also been reported[1,3] that brominated $(SN)_x$ may be sublimed to form brominated $(SN)_x$ films, analogous to the behavior of $(SN)_x$.[4] Recent work by Smith et al.[5] has shown that the major gas-phase species of $(SN)_x$ is a noncyclic $(SN)_4$ isomer having properties quite different from tetrasulfur tetranitride, S_4N_4. The $(SN)_4$ isomer spontaneously polymerizes on cool surfaces to form $(SN)_x$ films.[5]

We have studied the vapor-phase species using a variety of mass spectrometric techniques in order to identify the vapor-phase species formed upon sublimation of $(SNBr_{0.4})_x$, to better understand the mechanism of bromination and vaporization, and to characterize the species involved in film formation. Additionally, we have examined the vapor-phase species of the analogous compounds formed when S_4N_4 is halogenated with Br_2 and ICl and when S_4N_4 is brominated in CS_2 solution. Brominated S_4N_4 is of particular interest since work reported elsewhere[6] has found physical and chemical properties nearly indistinguishable from those of $(SNBr_{0.4})_x$. In the present work, we identify the major gas-phase species for each of these compounds and show that the spectra of brominated $(SN)_x$ and brominated S_4N_4 are nearly identical.

Experimental Section

Samples of $(SN)_x$ and S_4N_4 modified by reaction with Br_2 and ICl were prepared as described previously.[1,3]

Two mass spectrometers were used in this study. The first was a modulated molecular beam instrument with two regions of differential pumping, equipped with an Extranuclear Laboratories

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crossed-beam analyzer and quadrupole mass filter and designed to operate in both the crossed-beam and axial modes. Samples to be studied were placed in a Teflon Knudsen cell which may be operated at temperatures between 20 and 200 °C. The molecular beam effusing through a 1-mm orifice into the first differentially pumped region (maintained at $\leq 10^{-1}$ Torr) is directed at a molecular beam skimmer, which allows a well-collimated molecular beam to enter the analyzer section. The molecular beam is modulated using a rotating toothed wheel and subsequently passes through the ion source. The molecular-beam technique allows one to study unstable or reactive species in the effusive beam because of the total absence of surface-related phenomena; the molecules studied do not collide with surfaces after leaving the Knudsen cell. Modulation of the beam allows the complete elimination of background species from the mass spectra. Mass spectra were obtained at 10, 15, 20, 25, 70, and 100 eV and at temperatures from 40 to 150 °C. Individual samples were examined over extended periods (up to 12 h) to identify species which may be selectively volatilized. The technique of phase-angle spectrometry was used to determine the molecular weight of the gas-phase species obtained by sublimation of brominated $(SN)_x$ and halogenated S_4N_4 samples.[5] In this technique, the distance between the chopper and the ionizer is increased from 1 to 16 cm. The phase shifts resulting from the mass-dependent flight times of molecular species are related to the molecular weight after calibration with known species.

Electron impact (EI) and chemical ionization (CI) mass spectra were also obtained using a Hewlett-Packard 5980A mass spectrometer equipped with a dual EI-CI source and a conventional-solids inlet probe. Argon, methane, isobutane, and ammonia were used as CI reagents. The total pressure in the source was approximately 1 Torr in these experiments and all spectra were obtained using an electron energy of 70 eV.

Results

The mass spectra obtained using a conventional ion source and 70-eV EI ionization conditions gave spectra of brominated $(SN)_x$ and brominated S_4N_4 which are essentially indistinguishable. Figure 1(a) shows the spectra obtained for brominated $(SN)_x$ at 120 °C under these conditions. Both the brominated $(SN)_x$ and brominated S_4N_4 show distinct multiplets centered at approximately m/e 358, 438, and 520, with the series of peaks around m/e 358 the most intense. These multiplets may be ascribed to one or more compounds con-