orbital population compared to the ester according to previous interpretations.[28] The decrease in $\nu(^{75}\text{As})$ at 77°K compared to 298°K is normal behavior based on theory presented by Bayer.[31] The value of the electric field gradient asymmetry parameter, η, found in $Sb(SC_6H_5)_3$ suggests that the threefold axis of the molecule is retained to a reasonable degree.

Finally, in looking for ^{35}Cl signals in *p*-chlorophenyl group Va esters we found the ^{35}Cl resonances in $(p\text{-}ClC_6H_4S)_2$ at 34.07 (5), 34.28 (5), and 34.48 (5) MHz. These frequencies are almost identical with those found in meta and para chlorine atoms in substituted triphenylarsines and -stibines.[29] The ^{35}Cl signal in $NaSC_6H_4Cl$ was found at 34.55 (18) MHz for comparison.[32]

Registry No. $AsCl_3$, 7784-34-1; $SbCl_3$, 10025-91-9; C_2H_5OH, 64-17-5; C_3H_7OH, 71-23-8; $(CH_3)_2CHOH$, 67-63-0; C_4H_9OH, 71-36-3; $(CH_3)_3COH$, 75-65-0; C_6H_5OH, 108-95-2; *p*-$CH_3C_6H_4OH$, 106-44-5; C_2H_5SH, 108-98-5; C_3H_7SH, 107-03-9; $(CH_3)_2CHSH$, 75-33-2; $(CH_3)_3CSH$, 75-66-1; CH_3OH, 67-56-1; C_6H_5SNa, 930-69-8; *p*-$CH_3C_6H_4SNa$, 10486-08-5; *p*-ClC_6H_4SNa, 18803-44-6; C_4H_9SH, 109-79-5; C_6H_5SeNa, 23974-72-3; $C_6H_5SeSeC_6H_5$, 1666-13-3; $As(OCH_3)_3$, 6596-95-8; $As(OC_2H_5)_3$, 3141-12-6; $As(OC_3H_7)_3$, 15606-91-4; $As(OC_4H_9)_3$, 3141-10-4; $As[OCH(CH_3)_2]_3$, 39936-83-9; $As[OC(CH_3)_3]_3$, 23060-64-2; $As(OC_6H_5)_3$, 1529-86-8; $As(SC_2H_5)_3$, 34666-79-0; $As(SC_3H_7)_3$, 5582-57-0; $As[SCH(CH_3)_2]_3$, 39936-86-2; $As[SC(CH_3)_3]_3$, 39971-63-6; $As(SC_6H_5)_3$, 1776-70-1; $As(SC_6H_4CH_3)_3$, 39936-88-4; $Sb(OC_2H_5)_3$, 10433-06-4; $Sb(OC_3H_7)_3$, 4292-34-6; $Sb(OC_4H_9)_3$, 2155-74-0; $Sb[OCH(CH_3)_2]_3$, 18770-47-3; $Sb[OC(CH_3)_3]_3$, 10433-03-1; $Sb(SC_6H_5)_3$, 28609-58-7; $As(OC_6H_4CH_3)_3$, 1529-85-7; $As(SC_6H_4Cl)_3$, 39936-95-3; $Sb[SCH(CH_3)_2]_3$, 22141-93-1; $Sb(SC_4H_9)_3$, 22082-51-5; ^{35}Cl, 13981-72-1; ^{75}As, 7440-38-2; ^{121}Sb, 14265-72-6; ^{123}Sb, 14119-16-5.

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(31) H. Bayer, *Z. Phys.*, 130, 227 (1951).

(32) Note Added in Proof. After acceptance of this paper, mass spectra of several arsenites and thioarsenites were reported [P. Froyen and J. Moller, *Org. Mass Spectrom.*, 7, 73 (1973)]. The assignments and fragmentation patterns are essentially in agreement with those found here.

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Mossbauer and Nuclear Quadrupole Resonance Spectra of Some Unsymmetrical Organoantimony Compounds and Nuclear Quadrupole Resonance Spectra of Some of the Arsenic Analogs

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Unsymmetrical stibines of the type $(C_6H_5)_2Sb(CH_2)_nSb(C_6H_5)_2$ show little or no asymmetry in the electric field gradient about the antimony nucleus. Large asymmetry is observed in cases where the diphenylstibino group is attached to Cl or is bound to an acetylenic linkage. This behavior is reminiscent of the occurrence of nuclear quadrupole splitting in tetravalent tin compounds and both phenomena may well arise from a common factor(s)—interaction of p electrons of the X group or polarity of the σ bonds. ^{121}Sb Mossbauer spectra of trimethylstibine and the nqr spectra of $(C_6H_5)_2AsCH_2As(C_6H_5)_2$ and *p*-$(C_6H_5)_2AsCH_2C_6H_4CH_2As(C_6H_5)_2$ have also been reported. The bond between As (or Sb) and the methylene group is electronically similar to that between As (or Sb) and the phenyl group.

Introduction

Recently, Semin, *et al.*,[1] reported nqr spectra for two symmetrical stibines, trimethylstibine and tris(*trans*-2-chlorovinyl)stibine, and for two unsymmetrical compounds, diphenylchlorostibine and bis(diphenylstibino)acetylene. The unsymmetrical compounds were found to have increased quadrupole splitting (e^2qQ/h for ^{121}Sb, ^{123}Sb respectively (MHz): 769, 980; 569.4, 726.2) as compared to the symmetrical compounds (e^2qQ/h for ^{121}Sb, ^{123}Sb (MHz): for $(CH_3)_3Sb$, 493.4, 630.6; for $(trans\text{-}ClHC{=}CH)_3Sb$, 533.0, 679.4; for $SbCl_3$, 383.6, 488.8). In addition, the unsymmetrical compounds were found to have very large asymmetry parameters ($\eta_{^{121}Sb} = \eta_{^{123}Sb}$ is 0.825 for $(C_6H_5)_2SbCl$ and 0.499 for $(C_6H_5)_2SbC{\equiv}CSb(C_6H_5)_2$). These results were ascribed to the highly asymmetric electron distribution around the Sb atom which in turn was attributed to the unsymmetrical substitution about antimony.

As part of a study of the stability of aromatic arsines and stibines as compared with the aliphatic analogs, we have determined ^{75}As or $^{121,123}Sb$ nqr spectra and ^{121}Sb Mossbauer spectra for several unsymmetrical arsines and stibines of the type $(C_6H_5)_2E\text{-}R\text{-}E(C_6H_5)_2$ (where E = As or Sb and R = CH_2, $(CH_2)_4$, $(CH_2)_{10}$, or $CH_2C_6H_4CH_2$) for comparison with spectra of symmetrical arsines and stibines, *e.g.*, $(C_6H_5)_3As$, $(C_6H_5)_3Sb$, and $(CH_3)_3Sb$. These results are reported below and it is to be particularly noted that the nqr frequencies, the quadrupole splittings, and the asymmetry parameters for these unsymmetrical stibines, in contrast to the values reported by Semin, *et al.*,[1] are very similar to those found for symmetrical stibines.[2,3]

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(1) G. K. Semin, E. V. Bryukhova, T. A. Babushkina, V. I. Svergun, A. E. Borisov, and N. V. Novikova, *Iv. Akad. Nauk SSSR, Ser. Khim.*, 1183 (1972).

(2) T. B. Brill and G. G. Long, *Inorg. Chem.*, 11, 225 (1972).

(3) (a) R. G. Barnes and P. J. Bray, *J. Chem. Phys.*, 23, 407 (1955); (b) *ibid.*, 23, 1177 (1955).

Table I. Compounds and Analytical Data

Compd	Ref	Analytical data: Mp, °C							
		Mp, °C		% carbon		% hydrogen		% As or Sb	
		Lit.	Obsd	Calcd	Found	Calcd	Found	Calcd	Found
Methylenebis(diphenylarsine)	4	96–97	95–97	63.59	63.30	4.70	4.46	31.73	31.84
α,α′-*p*-Xylenebis(diphenylarsine)	*a*		129 dec	68.34	68.18	5.02	5.04	26.64	26.27
Methylenebis(diphenylstibine)	*a*		76–78	53.06	53.24	3.92	3.84	43.02	42.55
Tetramethylenebis(diphenylstibine)	6	108[b]	70–72[b]	55.31	55.37	4.64	4.50	40.05	39.86
Decamethylenebis(diphenylstibine)	*a*		53–55	59.00	58.71	5.82	5.69	35.18	34.87

[a] Previously unreported compound. [b] The melting point does not agree with that previously reported. The methylene pmr spectrum for our compound is in accord with that expected for $(C_6H_5)_2Sb(CH_2)_4Sb(C_6H_5)_2$. We have prepared the tetrabromide derivative which melts with decomposition in the range 160–167° (lit.[6] mp 164–165°) and has the antimony analysis: calcd, 26.25%; found, 26.52%.

Table II. Arsenic and Antimony Nqr Data[a] (MHz) at 300°K for Some Arsines and Stibines

Compd	$\nu(^{75}As)$	$\nu(^{121}Sb)$		$\nu(^{123}Sb)$		
	$^3/_2 \leftrightarrow {}^1/_2$	$^5/_2 \leftrightarrow {}^3/_2$	$^3/_2 \leftrightarrow {}^1/_2$	$^3/_2 \leftrightarrow {}^1/_2$	$e^2qQ/h(^{121}Sb)$	$\eta(Sb)$
$(C_6H_5)_3As$[b]	97.05					
$(C_6H_5)_2AsCH_2As(C_6H_5)_2$	98.26 (12)					
	96.11 (12)					
p-$(C_6H_5)_2AsCH_2C_6H_4CH_2As(C_6H_5)_2$	94.93 (10)					
$(C_6H_5)_3Sb$[c]		150.2 (20)	75.51 (20)	46.54 (20)	501.0	0.09
		153.1 (20)	76.57 (20)	46.70 (20)	510.4	0.03
$(C_6H_5)_2SbCH_2Sb(C_6H_5)_2$		148.1 (3)	75.44 (3)		495.0	0.12
		146.2 (3)	73.79 (3)		488.1	0.09
$(C_6H_5)_2Sb(CH_2)_4Sb(C_6H_5)_2$		145.0 (5)	74.53 (3)	47.40 (2)	485.8	0.14

[a] Parenthetical numbers are signal-to-noise ratios. [b] An average of four closely spaced resonance frequencies as reported in ref 3a. [c] In agreement with results reported in ref 3b.

Table III. ^{121}Sb Mossbauer Data

Compd	Isomer shift *vs.* InSb, mm/sec (±0.05)	e^2qQ/h		Width, mm/sec (±0.05)	Fractional intens[a]	
		mm/sec (±0.5)	MHz (±15)		$\Delta m = 0$	$\Delta m = 0$
$(C_6H_5)_3Sb$	−0.61	17.0	509	2.60	0.202	0.163
$(C_6H_5)_2SbCH_2Sb(C_6H_5)_2$	−0.69	17.5	524	2.47	0.272	0.227
$(C_6H_5)_2Sb(CH_2)_4Sb(C_6H_5)_2$	−0.50	16.9	506	2.40	0.353	0.242
$(C_6H_5)_2Sb(CH_2)_{10}Sb(C_6H_5)_2$	−0.57	17.7	530	2.34	0.280	0.229
$(CH_3)_3Sb$	−0.22	16.3	488	2.24	0.179[a]	

[a] With the exception of trimethylstibine, improved fit of the data points was obtained by allowing the $\Delta m = 0$ and $\Delta m = 1$ transitions to have different fractional intensities. This procedure gave no improvement in the fitting of the trimethylstibine and hence the reported data were generated from a fit with the transition probabilities governed by Clebsch–Gordon coefficients.

Experimental Section

Syntheses. Triphenylarsine and triphenylstibine, obtained from M and T Chemicals, Inc., Rahway, N. J., were recrystallized from ethanol prior to use. Some of the $(C_6H_5)_2E$–R–$E(C_6H_5)_2$ compounds have been previously reported;[4–6] others are new. All of these compounds are listed in Table I along with analytical data. They were prepared by reaction of $NaE(C_6H_5)_2$, made in liquid ammonia from sodium and $(C_6H_5)_3E$, and the appropriate dichloro- or dibromoalkane. The cleavage of $(C_6H_5)_3E$ was facilely effected in 30–45 min. Phenylsodium was destroyed by adding the theoretical amount of ammonium chloride. Yields and purity of the crude products depended upon avoiding excess dihaloalkane. The α,α′-*p*-xylenebis(diphenylarsine) was purified by slurrying and washing the crude compound with hot ethanol. The other compounds were recrystallized from ethanol. The solid compounds are air sensitive and were stored *in vacuo*; reaction with oxygen of the air is slow however, so that the compounds can be handled for short times on the bench top.

Trimethylstibine was prepared from trimethylantimony dibromide and granulated zinc by the procedure of Morgan and Yarsley.[7] The product showed a single nmr signal in $DCCl_3$ solution at δ 0.70 ppm.

Nqr Spectra. The spectrometer system used to determine the ^{75}As, ^{121}Sb, and ^{123}Sb nqr data, reported in Table II, has been previously described.[8] The complete five-line spectrum was not observed in any of the $(C_6H_5)_2Sb$–$(CH_2)_n$–$Sb(C_6H_5)_2$ compounds. However, in tetramethylenebis(diphenylstibine), the $^3/_2 \leftrightarrow {}^1/_2$ transition for ^{123}Sb lies at the precise frequency expected in light of the assignments made for the ^{121}Sb lines. By use of this fact and by analogy to the closely related compounds triphenylstibine and triarylstibine,[2] assignments can be made confidently. The error in the resonance frequencies is estimated to be 0.01 MHz as a result of the uncertainty in assigning the center line of the resonance multiplet. Nqr signals were not observed for decamethylenebis(diphenylstibine).

Mossbauer Spectra. Antimony-121 Mossbauer spectra were determined on the compounds listed in Table III with equipment and procedures which essentially have been previously described.[9] The following modifications and details need be noted. Absorbers were prepared which had 10 mg of Sb/cm² by mixing appropriate quantities of the antimony compound with powdered polyethylene. The concentration of antimony in the trimethylstibine absorber was only approximately 10 mg of Sb/cm² but was not accurately determined since the compound is extremely air sensitive and the absorber had to be prepared in an inert atmosphere. The liquid helium cryostat, fabricated by Kontes-Martin, Evanston, Ill., was patterned after the design of Zabransky and Ruby[10] but modified so that source and absorber are immersed in helium gas at 1 atm surrounded by a chamber containing liquid helium. Thus, spectra were determined at 1 atm with both absorber and the $Ni_{21}{}^{121}Sn_2B_6$ (^{121}Sb) source[11] cooled at 4°K. The isomer shift (IS) of an InSb standard was carefully determined seven times and found to be −1.68 ± 0.02 mm/sec at both 4 and 80°K; isomer shifts in Table III have been reported with respect to InSb by subtracting this value from the experimental ones. Runs were made for 10–12-hr duration which permitted collection of about 50,000 counts per folded velocity point. As usual,[9] data points were fit to an eight-line quadrupole split pattern. Signifi-

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(5) A. Tzschach and W. Lange, *Chem. Ber.*, **95**, 1360 (1962).

(6) G. H. Cookson and F. G. Mann, *J. Chem. Soc.*, 2895 (1949).

(7) G. T. Morgan and V. E. Yarsley, *J. Chem. Soc.*, **127**, 184 (1925).

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(9) G. G. Long, J. G. Stevens, R. J. Tullbane, and L. H. Bowen, *J. Amer. Chem. Soc.*, **92**, 4230 (1970).

(10) B. J. Zabransky and S. L. Ruby, *Rev. Sci. Instrum.*, **41**, 1359 (1970).

(11) L. H. Bowen, *et al.*, in "Mossbauer Effect Methodology," I. J. Gruverman, Ed., Vol. 7, Plenum Press, New York, N. Y., 1971, p 233.

cant improvement in the fitting of the data, as evidenced by an improved χ^2 value, was obtained in most cases by permitting the $\Delta m = 0$ and $\Delta m = 1$ transitions to have different relative intensities, as compared to the usual fit of data in which all transition intensities are governed by Clebsch-Gordon coefficients. This suggests that either these compounds show a Goldanskii-Karyagin effect, or possibly, at these large absorptions, unequal saturation of the $\Delta m = 0$ and $\Delta m = 1$ lines occurs. The method of absorber preparation, which intimately mixes the powdered compound with powdered polyethylene, makes orientation of the microcrystals an unlikely cause of the observed intensity effect.

We previously reported Mossbauer data for triphenylstibine which had been determined with the source and spectrometer at Argonne National Laboratory (IS = −9.69 mm/sec relative to the $Ca^{121}SnO_3$ (^{121}Sb) source, which corresponds to −1.3 mm/sec relative to InSb; $e^2qQ/h = +17.5$ mm/sec).[9] We have now redetermined the spectrum for this compound (Table III) on the spectrometer at North Carolina State University, so that (a) the data in Table III would be directly comparable without use of conversion factors for the different sources and (b) with our alloy source, the absorption of triphenylstibine will fall near zero velocity and give a more precise IS value. Indeed, the quadrupole splittings are essentially identical in both determinations of the spectrum, but the isomer shifts differ by 0.7 mm/sec. Comparison of absolute isomer shift values obtained with different sources, instruments, and calibration methods is always difficult, and especially at the velocity ranges observed for ^{121}Sb. It is clear that measurements made on a variety of compounds with the same source and spectrometer permit the best comparison of isomer shift data on a relative scale.

Results and Discussion

Arsines. Nqr frequencies for the two unsymmetrical arsines, $[(C_6H_5)_2As]_2CH_2$ and p-$[(C_6H_5)_2AsCH_2]_2C_6H_4$, are listed in Table II. Since ^{75}As has a nuclear spin angular momentum quantum number of $^3/_2$, only one nqr transition is possible and hence does not permit the simultaneous calculation of quadrupole coupling constants and asymmetry parameters. These nqr frequencies are not markedly different from those observed for triphenylarsine[3] and for para-substituted triarylarsines[2] which suggests that the bond between As and the methylene group is electronically similar to a bond between As and a phenyl group. It is interesting to note that the nqr spectra both of bis(diphenylarsino)methylene and of the antimony analog consist of two signals (about 2 MHz apart) which implies two crystallographically different sites and suggests that the two compounds are isostructural.

Stibines. Although two and three nqr frequencies are expected, respectively, for the naturally occurring isotopes of antimony (^{121}Sb and ^{123}Sb), the transition intensities are not equal, with the result that in numerous cases only part of the five-line spectrum is observed.[2] If as many as two frequencies are located for an isotope, the quadrupole coupling constant, e^2qQ/h, and the electric field gradient asymmetry parameter, η, can be calculated. For ^{121}Sb the Mossbauer spectrum also may be observed, which, in addition to the isomer shift (IS) parameter, permits determination of the quadrupole coupling constant (when $|e^2qQ/h| > \sim 150$ MHz) and the asymmetry parameter (when $\eta > \sim 0.2$). The values obtained for e^2qQ/h and η from ^{121}Sb Mossbauer spectra are not nearly as accurate as those obtained by nqr spectroscopy, but data can be obtained for compounds which fail to yield nqr signals. ^{121}Sb and ^{123}Sb nqr data (frequencies, quadrupole splittings, and asymmetry parameters) and ^{121}Sb Mossbauer data (isomer shifts, quadrupole splittings, widths, and intensities) are recorded in Tables II and III.

Symmetrical Stibines. The simplest compound studied here is trimethylstibine, which has an ^{121}Sb isomer shift of −0.22 mm/sec and quadrupole coupling constant of 488 MHz as determined from the Mossbauer spectrum (in good agreement with the value determined from nqr[1]). In this symmetrical molecule, the z axis is the threefold symmetry axis and the positive sign of e^2qQ/h indicates that excess p-electron density lies along this axis. This is equivalent to saying that p_x and p_y orbitals have been used in forming bonds to a greater extent than the p_z orbital. Further, the large magnitude of the coupling constant implies that the lone pair must have appreciable p character. The data are in accord, thus, with a σ-bonded model in which the antimony is essentially sp^3 hybridized except that the lone-pair orbital has somewhat more than 25% s character and the orbitals involved in bonding have somewhat greater than 75% p character. This would seem to be borne out by bond angles in related compounds: 100° in $(CF_3)_3Sb$,[12] 102° in both $(p\text{-}CH_3C_6H_4)_3As$[13] and $(2,4\text{-}(CH_3)_2C_6H_4)_3As$.[14]

Comparison of the data for triphenylstibine with those for trimethylstibine shows, rather surprisingly, that both the isomer shifts and the nuclear quadrupole coupling constants are very similar. The phenyl group is somewhat more electronegative than a methyl group and thereby is more effective in withdrawing p_x- and p_y-electron density. This is reflected in the increase in nuclear quadrupole coupling constant, and, including data for tris(*trans*-2-chlorovinyl)stibine,[1] the order of increasing e^2qQ/h is $CH_3 < C_6H_5 <$ *trans*-ClCH=CH–, which also should be the order of increasing electronegativity of these groups. The values of e^2qQ/h for all three compounds fall between 488 and 533 MHz. One probably should infer that this represents only small differences in withdrawal of p-electron density since different crystallographic sites in triphenylstibine cause ~10-MHz difference in the quadrupole coupling constant. The isomer shift for triphenylstibine is −0.61 mm/sec, a little more negative than that for trimethylstibine, which implies that either the antimony in triphenylstibine has slightly greater s-electron density or that there has been removal of considerable p-electron density, thereby deshielding the antimony nucleus. The similarity of the e^2qQ/h values for the two compounds makes the latter possibility unlikely, so for triphenylstibine, we must look for a bonding model that keeps the p-electron density about the same as that for trimethylstibine, but allows the s-electron density at antimony to be somewhat larger in the former compound. A model that would accomplish this is to allow a small amount of backdonation of electrons from the ring π system into orbitals made from higher energy states on Sb (s and d); *i.e.*, the overall bonding picture need include a contribution of the type

Only a small contribution of this sort would be needed to account for the small IS difference; however this back-donation could explain, at least in part, the greater stability of triphenylstibine as compared with that of the methyl analog.[15] It should be noted that the difference in IS between $(C_6H_5)_3Sb$ and $(CH_3)_3Sb$ is, although small, more pronounced and in the opposite direction from the difference observed between triphenyl- and trimethylantimony dihalides.[9]

Unsymmetrical Stibines, $(C_6H_5)_2SbX$. Upon substitution of an X group for a phenyl group in triphenylstibine, one would anticipate not only changes in isomer shifts, nqr frequencies, and quadrupole coupling constants in accord with the nature of X, but also the loss of axial symmetry which

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[13] J. Trotter, *Can. J. Chem.*, 41, 14 (1963).

[14] J. Trotter, *Acta Crystallogr.*, 16, 1187 (1963).

[15] H. A. Skinner, *Advan. Organometal. Chem.*, 2, 49 (1964).

could give rise to nonzero values of η, the electric field asymmetry parameter. Indeed, Semin, *et al.*,[1] observed large values of η for $(C_6H_5)_2SbCl$ and $(C_6H_5)_2SbC{\equiv}CSb(C_6H_5)_2$. For compounds of the type $(C_6H_5)_2Sb\text{-}R\text{-}Sb(C_6H_5)_2$ (*cf.* Tables II and III) the fits for the Mossbauer spectra are not improved by inclusion of nonzero η values, and the nqr spectra give η values of the same order of magnitude as found for triphenylstibine itself—presumably associated with molecular distortion resulting from packing forces. This is in accord with the observation in the preceding paragraph that the antimony nucleus sees little difference between a phenyl substituent and a methyl substituent, now expanded to include a methylene substituent. Indeed, isomer shifts and quadrupole splittings for trimethylstibine, triphenylstibine, and all of the bis(diphenylstibino)methylene compounds also are similar; IS ranges from −0.22 to −0.69 mm/sec and e^2qQ/h ranges from 486 to 530 MHz.

Although based upon very limited observations, it is interesting to note that $\eta \cong 0$ when X is attached to antimony through an aliphatic linkage and that η is large when X has considerable electron density in p orbitals, lone pairs in the case of chlorine, electrons associated with the triple bond in the case of the acetylenic group.[16] The similarity of this behavior of η to the behavior of e^2qQ/h in tin compounds of the R_3SnX type is striking.[17-19] In the tin case, when R = C_6H_5 or CH_3 and if X is a halogen, oxygen, or acetylenic linkage, e^2qQ/h has a large value (neither its sign nor the value of η can be determined from ^{119}Sn Mossbauer spectra without application of an external magnetic field), whereas if X is an ethylenic or methylenic linkage, e^2qQ/h is essentially zero.[20] Although the quadrupole splitting in the Sn^{IV} compounds has been attributed to π interaction with nonbonded p electrons on the X group,[17] it has also been proposed that inequalities in σ-bond polarities can explain the magnitude of e^2qQ/h in Sn^{IV} compounds.[19] It may well be that the η values in unsymmetrical Sb^{III} compounds and the e^2qQ/h values in Sn^{IV} compounds are influenced by common factors.

Registry No. $(C_6H_5)_2AsCH_2As(C_6H_5)_2$, 21892-63-7; *p*-$(C_6H_5)_2AsCH_2C_6H_4CH_2As(C_6H_5)_2$, 39936-99-7; $(C_6H_5)_3Sb$, 603-36-1; $(C_6H_5)_2SbCH_2Sb(C_6H_5)_2$, 30224-53-4; $(C_6H_5)_2Sb(CH_2)_4Sb(C_6H_5)_2$, 5865-82-7; $(C_6H_5)_2Sb(CH_2)_{10}Sb(C_6H_5)_2$, 39937-02-5; $(CH_3)_3Sb$, 594-10-5; ^{75}As, 7440-38-2; ^{121}Sb, 14265-72-6; ^{123}Sb, 14119-16-5.

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[16] This is also the case for bis(diphenylantimony) oxide where $\eta = 0.90 \pm 0.05$! This value was taken from the ^{121}Sb Mossbauer spectrum of the compound which was determined on the same equipment and under the same conditions as used for the spectra reported in this paper. The other Mossbauer parameters for ^{121}Sb are IS = -1.10 ± 0.05 mm/sec and $e^2qQ/h = 21 \pm 1$ mm/sec: L. H. Bowen, J. G. Stevens, and G. G. Long, to be submitted for publication.

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[19] R. V. Parish and R. H. Platt, *J. Chem. Soc. A*, 2145 (1969).

[20] The large positive e^2qQ/h in the stibines is due to the unshared electron pair, which, of course, is not present in the Sn^{IV} compounds.

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Potentiometric Study of the Systems KCl-AlCl$_3$ and KCl-AlCl$_3$-ZnCl$_2$ at 300°, Performed with a Chlorine-Chloride Electrode

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A completely sealed off chlorine-chloride electrode cell was developed. By means of this cell a KCl-AlCl$_3$ melt saturated with KCl was found to contain 51.69 ± 0.03 mol % KCl at 300°. The pK value for the dissociation $2AlCl_4^- \rightleftharpoons Al_2Cl_7^- + Cl^-$ was found to be 7.83 ± 0.02 at 300°. At very high chloride activities (*i.e.*, low pCl$^-$) added Zn(II) formed $ZnCl_4^{2-}$, while at somewhat lower chloride activities the buffering effect of adding 0.10 and 0.30 *F* ZnCl$_2$ to KCl-AlCl$_3$ could best be explained by the following dissociation: $ZnCl_4^{2-} \rightleftharpoons ZnCl_3^- + Cl^-$, where $ZnCl_3^-$ possibly is solvated to $AlCl_4^-$. The pK value of this reaction was found to be 2.15 ± 0.04 at 300°.

Introduction

It is well-known that pCl$^-$ plays a critical role in the intricate chemical phenomena that occur in chloride molten salts, and it has become common to try to describe this role quantitatively in terms of model acid-base equilibria in which the activity coefficients of the reacting species are treated as constants, independent of system composition. In such investigations the foremost problem is to establish reliable and convenient experimental procedures for measuring pCl$^-$. Once definitive data have been obtained, the utility and uniqueness of model equilibria with constant activity coefficients can be critically examined. These two tasks are the central concerns of the present investigation.

The particular acid-base phenomenon chosen for study was the buffering action of solute ZnCl$_2$ in KCl-AlCl$_3$ melts. The existence of this buffering action has been known for some years, and it proved very useful in investigations that led to the discovery of some of the novel low oxidation states of tellurium,[1] but its quantitative aspects have never been studied.

In the present paper we describe a relatively simple concentration cell with chlorine electrodes and report the pCl$^-$ dependence on composition of the molten system KCl-AlCl$_3$-ZnCl$_2$ at low ZnCl$_2$ concentration and KCl:AlCl$_3$ mole ratios neighboring unity. Then, using these data, we

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[1] N. J. Bjerrum, *Inorg. Chem.*, 9, 1965 (1970); 10, 2578 (1971); 11, 2648 (1972).