ticularly low C–S bond energy (1.97 eV) and preliminary results indicate that this may be a useful source of CF_3 radicals.[27]

(27) W. R. Cullen and D. C. Frost, unpublished results.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY
NORTH CAROLINA STATE UNIVERSITY, RALEIGH, NORTH CAROLINA 27607

Studies of Pentavalent Organoarsenic, -antimony, and -bismuth Halide Compounds by Nuclear Quadrupole Resonance Spectroscopy

BY T. B. BRILL[1] AND G. G. LONG

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The ^{75}As, ^{121,123}Sb, ^{209}Bi, ^{35,37}Cl, and ^{79,81}Br nqr spectra have been recorded in pentavalent organo group Va halide compounds having stoichiometry R_3MX_2, where R = CH_3, $C_6H_5CH_2$, and C_6H_5; X = F, Cl, and Br; and M = As, Sb, and Bi. All compounds studied, except for trimethylarsenic dibromide, appear to have trigonal-bipyramidal geometry in the solid state with idealized D_{3h} symmetry. $(CH_3)_3AsBr_2$ may be saltlike as $(CH_3)_3AsBr^+Br^-$ with the cation having C_{3v} symmetry. Electronic inductive effects have been interpreted in all compounds in terms of variation in the p orbital occupation in the group Va elements and the halogens. Nucleophilic character of the constituent atoms and groups is as follows: Bi > Sb > As, Br > Cl > F, and $CH_3 > C_6H_5CH_2 > C_6H_5$. Data for the pentavalent arsenic compounds are compared to those in R_3As where R = C_6H_5 and $C_6H_5CH_2$. The extra pair of electrons in As(III) compared to As(V) possesses considerable p character which helps to explain the pyramidal geometry assumed in the R_3As compounds.

Introduction

Arsenic, antimony, and bismuth form a series of pentavalent compounds having the stoichiometry R_3MX_2 where R may be alkyl or aryl groups and X the halides. Since all of the above three group Va elements and several of the halogens have quadrupole nuclei, nuclear quadrupole resonance spectroscopy is likely to be very useful in further elucidating the chemistry of these compounds. Until now, however, few nqr data have appeared concerning this particular class of compounds. Parker[2a] recorded the halogen and several antimony resonances in $(CH_3)_3SbX_2$ (X = Cl, Br, I) compounds. Macalady[2b] began preliminary studies on triphenylantimony dichloride but the several resonances he found were measured only approximately and no value of the electric field gradient asymmetry parameter could be determined. These data are apparently the only nqr results for Sb(V) organometallics heretofore reported. No ^{75}As resonances in pentavalent organoarsenic(V) compounds have been reported and, in fact, it appears that the only other As(V) resonance known is that in $Na_2HAsO_4 \cdot 7H_2O$.[3] The pentavalent state is an uncommon oxidation number for bismuth and the fact that no other Bi(V) nqr signals have been previously reported is not surprising. Barnes and Bray[4] found arsenic and antimony resonances in $(C_6H_5)_3As$ and $(C_6H_5)_3Sb$. Robinson, Dehmelt, and Gordy[5] found bismuth resonances in $(C_6H_5)_3Bi$.

Muetterties and Phillips[6] have suggested that in pentacoordinate compounds of the R_3MX_2 type the more electronegative atoms (the halogens) are situated on the two apical positions of a trigonal-bipyramidal structure while the less electronegative groups link with the central atom at the three equatorial positions. The trigonal bipyramidal geometry has idealized D_{3h} point group symmetry according to Figure 1.

For the antimony compounds, Wells[7] has determined by X-ray diffraction that the $(CH_3)_3SbX_2$ compounds (X = Cl, Br, I) take on the idealized D_{3h} symmetry in the solid state. The nqr data[2a] are in agreement with this since the asymmetry parameter of the antimony electric field gradient is very close to zero. Polynova and Porai-Koshits[8] found that the structure of $(C_6H_5)_3SbCl_2$ is also a trigonal bipyramid about the antimony atom. The ir spectra of the trimethylantimony dihalides[9] and triphenylantimony dihalides[10] are consistent with the D_{3h} point group. No data have been reported to date on the structural aspects of the tribenzylantimony dihalide compounds.

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(1) To whom inquiries should be addressed at the Department of Chemistry, University of Delaware, Newark, Del. 19711.

(2) (a) D. J. Parker, Ph.D. Dissertation, University of Wisconsin, 1959; (b) D. L. Macalady, Ph.D. Dissertation, University of Wisconsin, 1969.

(3) E. D. Jones and E. A. Uehling, *J. Chem. Phys.*, **36**, 1690 (1962).

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

(5) H. G. Robinson, H. G. Dehmelt, and W. Gordy, *Phys. Rev.*, **89**, 1305 (1953).

(6) E. L. Muetterties and W. D. Phillips, *J. Amer. Chem. Soc.*, **81**, 1084 (1959).

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(8) T. N. Polynova and M. A. Porai-Koshits, *J. Struct. Chem. (USSR)*, **7**, 691 (1966).

(9) G. G. Long, G. O. Doak, and L. D. Freedman, *J. Amer. Chem. Soc.*, **86**, 209 (1964).

(10) G. O. Doak, G. G. Long, and L. D. Freedman, *J. Organometal. Chem.*, **4**, 82 (1965); K. M. Mackay, and D. B. Sowerby, *Spectrochim. Acta, Part A*, **24**, 611 (1968).

TABLE I

ARSENIC AND HALOGEN NQR FREQUENCIES IN R_3AsX_2 COMPOUNDS AT 300°K[a]

Compounds	$\nu(^{75}As)$	$\nu(^{35}Cl)$	$\nu(^{37}Cl)$	$\nu(^{70}Br)$	$\nu(^{81}Br)$
$(CH_3)_3AsF_2$	135.19 (120)				
$(CH_3)_3AsCl_2$	133.09 (70)	16.486 (15)	12.990 (3)		
$(CH_3)_3AsBr_2$	93.938 (30)			*b*	*b*
$(C_6H_5CH_2)_3AsF_2$	127.50 (25)				
$(C_6H_5CH_2)_3AsCl_2$	121.82 (20)	17.324 (2)	...		
$(C_6H_5CD_2)_3AsCl_2$	122.04 (20)	17.315 (2)	...		
$(C_6H_5)_3AsF_2$	117.75 (40)				
$(C_6H_5)_3AsCl_2$	116.11 (30)	17.620 (2)	...		
$(C_6H_5)_3AsBr_2$	110.43 (40)			145.38 (20)	121.45 (20)
$(C_6H_5)_3As$[c]	98.900 (3)				
	98.500 (5)				
$(C_6H_5CH_2)_3As$	91.755 (8)				

[a] Resonance frequencies are in megahertz; parenthetical numbers are signal-to-noise ratios. [b] No resonances were found between 20 and 200 MHz. [c] Reported in ref 4a at 77°K.

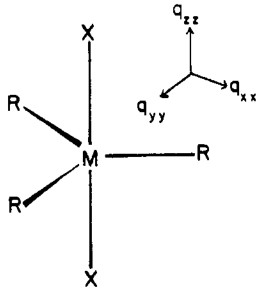

Figure 1.—The geometry of groups of R_3MX_2 compounds and the orientation of the electric field gradient principal axes for the M and X atoms.

On the basis of the rules of Gillespie and Nyholm[11] and by analogy to the corresponding antimony compounds, the arsenicc ompounds are expected to be trigonal bipyramids as well. Until only recently, however, very little spectroscopic information was available on the arsenic compounds. O'Brien, Doak, and Long[12] have studied the ir spectra of several and concluded that $(CH_3)_3AsF_2$, $(CH_3)_3AsCl_2$, and $(C_6H_5)_3AsF_2$ take on the trigonal-bipyramidal geometry. $(CH_3)_3AsBr_2$ appeared to be anomalous and O'Brien, *et al.*,[12] concluded that the compound is a salt, $(CH_3)_3AsBr^+Br^-$, in which the cation has C_{3v} symmetry. The structures of triphenylarsenic dichloride and dibromide and tribenzylarsenic difluoride and dibromide were not deduced from their ir spectra, but O'Brien[13] has indicated that the benzyl compounds probably have the trigonal-bipyramidal structure.

Triphenylbismuth dichloride has recently been the subject of an X-ray study[14] and it too has a trigonal-bipyramidal arrangement of groups about the bismuth atom. Jensen[15] has reported some ir spectral data for $(C_6H_5)_3BiBr_2$.

In the present work, the nqr spectra of ^{75}As, $^{121,123}Sb$, ^{209}Bi, $^{35,37}Cl$, and $^{79,81}Br$ nuclei in R_3MX_2 compounds have been recorded. Nqr spectroscopy can be used to gain further insight into structural questions in these compounds. Structural anomalies can conceivably be detected by comparing the resonance frequencies in related series of compounds. In addition, it is possible to observe simple electronic inductive effects which lead to information concerning the electronic structures of the atoms containing quadrupole nuclei. Comparison of the M(V) resonances in various compounds with one another and with similar M(III) systems leads to a more complete understanding of the electronic configurations in the two oxidation states of the central metalloids. Most of the discussion herein will be devoted to the arsenic compounds since the resonance frequency trends in these compounds are quite well defined. The antimony and bismuth compounds, as expected, show the same general effects.

Experimental Section

Synthesis.—Preparation and analyses of the compounds used in this study have been described before.[12,13,16] In general, Grignard reagents were added to the metal halides to form trivalent organometalloids. The pentavalent species were then obtained by direct halogenation for all compounds except the fluorides. The fluorides were prepared by a metathesis reaction with the chlorides. Care was taken to see that the compounds did not come into contact with moisture by keeping them in tightly sealed vials.

Nqr Spectra.—The nqr data reported in Tables I–III were recorded using a Wilks Scientific NQR-1A spectrometer. Frequency measurements were made with a Hewlett-Packard 5245L electronic counter by switching the superregenerative oscillator–detector to continuous wave operation. In several cases with the ^{75}As, $^{121,123}Sb$, and ^{209}Bi resonances, unusual line shapes were observed and determination of the center line of the resonance multiplet was difficult. Therefore, it is conceivable that an error of as much as 0.1 MHz could be present in several resonances. Frequency errors in Tables I–III are, however, about 0.01 MHz above 100 MHz and 0.003 MHz below 100 MHz barring the above possible source of larger error. In addition, since a superregenerative oscillator was used, it is virtually impossible to separate two closely spaced resonance frequencies. If two very slightly different sites should exist, the present interpretations would not be affected. Several compounds exhibited a large number of resonances. For example, a total of 14 signals was found in $(C_6H_5)_3BiBr_2$. Assignment of the frequencies is not a serious problem in view of the following frequency rela-

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(11) R. J. Gillespie and R. S. Nyholm, *Quart. Rev. Chem. Soc.*, **11**, 339 (1957).

(12) M. H. O'Brien, G. O. Doak, and G. G. Long, *Inorg. Chim. Acta*, **1**, 34 (1967).

(13) M. H. O'Brien, Ph.D. Dissertation, North Carolina State University, 1968.

(14) D. M. Hawley and G. Ferguson, *J. Chem. Soc. A*, 2539 (1968).

(15) K. A. Jensen and P. H. Nielson, *Acta Chem. Scand.*, **17**, 1875 (1963).

(16) G. O. Doak, G. G. Long, and M. E. Key, *Inorg. Syn.*, **9**, 92 (1967); A. Michaelis, *Justus Liebigs Ann. Chem.*, **320**, 141 (1902); I. P. Tsukervanik and D. Smirnov, *J. Gen. Chem.* (*USSR*), **7**, 1527 (1937); F. Challenger and A. T. Peters, *J. Chem. Soc.*, 2610 (1929).

TABLE II

ANTIMONY AND HALOGEN NQR DATA IN R_3SbX_2 COMPOUNDS AT 300°K[a]

Compound	$\nu(^{121}Sb)$		$\nu(^{123}Sb)$			e^2Qq/h		$\eta(Sb)$	$\nu(^{35}Cl)$	$\nu(^{37}Cl)$	$\nu(^{79}Br)$	$\nu(^{81}Br)$
	$\pm5/2 \rightleftarrows \pm3/2$	$\pm3/2 \rightleftarrows \pm1/2$	$\pm7/2 \rightleftarrows \pm5/2$	$\pm5/2 \rightleftarrows \pm3/2$	$\pm3/2 \rightleftarrows \pm1/2$	^{121}Sb	^{123}Sb					
$(CH_3)_3SbCl_2$	198.61(70)	99.327(70)[b]	180.95(10)	120.63(15)[b]	60.313(60)[b]	662.18	884.43	0.00	14.045(20)[b]	11.065(4)		
$(CH_3)_3SbBr_2$	189.03(10)	94.585(20)[b]	-	-	57.421(30)[b]	630.57	803.89	0.00			115.07(60)[b]	96.127(60)[b]
$(C_6H_5)_3SbF_2$	184.25(20)	92.592(25)	167.89(2)	111.69(8)	56.924(10)	603.91	769.90	0.065				
$(C_6H_5)_3SbCl_2$	177.29(25)	90.019(30)[c]	162.17(2)	107.17(10)	56.750(20)[c]	592.35	755.16	0.110	16.007(4)[c]	-		
									16.531(4)[c]	-		
$(C_6H_5)_3SbBr_2$	169.97(10)	85.193(8)	-	-	52.219(5)	565.78	720.93	0.043			127.05)18)	106.14(25)
$(C_6H_5CH_2)_3SbCl_2$	180.20(4)	90.087(6)	-	-	54.792(3)	600.58	763.34	0.00	-	-		
$(C_6H_5CH_2)_3SbBr_2$	-	88.195(3)	-	-	-	-	-	-			120.37(2)	100.56(3)
$(C_6H_5)_3Sb$[d]	156.200(5)	78.274(3)	142.174(2)	94.741(3)	47.841(3)	520.84	664.18	0.08				
	152.471(5)	76.912(3)	138.859(2)	92.267(3)	47.545(2)	509.00	648.56	0.08				

[a] Frequencies are in megahertz. Parenthetical numbers are signal-to-noise ratios. [b] Transition frequencies reported in ref 2a. [c] Transition frequencies reported in ref 2b. [d] Reported in ref 4b at 77°K.

TABLE III

BISMUTH AND HALOGEN NQR DATA IN $(C_6H_5)_3BiX_2$ COMPOUNDS AT 300°K[a]

Compound	$\nu(^{209}Bi)$				$e^2Qq/h(^{209}Bi)$	$\eta(^{209}Bi)$	$\nu(^{79}Br)$	$\nu(^{81}Br)$
	$\pm^9/_2 \rightleftarrows \pm^7/_2$	$\pm^7/_2 \rightleftarrows \pm^5/_2$	$\pm^5/_2 \rightleftarrows \pm^3/_2$	$\pm^3/_2 \rightleftarrows \pm^1/_2$				
$(C_6H_5)_3BiCl_2$	178.51 (6)	133.75 (15)	89.106 (14)	44.739 (25)	1069.9	0.020		
	173.23 (6)	129.72 (20)	86.257 (8)	44.044 (10)	1039.8	0.043		
$(C_6H_5)_3BiBr_2$	167.96 (3)	125.86 (12)	83.816 (3)	42.351 (15)	1007.2	0.032	111.90 (9)	93.488 (10)
	158.73 (3)	118.81 (12)	78.951 (3)	40.670 (8)	952.26	0.053	113.75 (5)	95.029 (5)
							116.05 (5)	96.950 (5)
$(C_6H_5)_3Bi$[b]	111.438	83.516	55.214	29.785	669.06	0.09		

[a] Parenthetical numbers are signal-to-noise ratios. Frequencies are in megahertz. [b] Resonances reported in ref 5.

tionships:[17] chlorine, $\nu(^{35}Cl)/\nu(^{37}Cl) = 1.269$; bromine, $\nu(^{79}Br)/\nu(^{81}Br) = 1.197$; antimony-121, $\nu(\pm^5/_2 \rightleftarrows \pm^3/_2)/\nu(\pm^3/_2 \rightleftarrows \pm^1/_2) \simeq 2$ for small η; antimony-123, $\nu(\pm^7/_2 \rightleftarrows \pm^5/_2)/\nu(\pm^5/_2 \rightleftarrows \pm^3/_2)/\nu(\pm^3/_2 \rightleftarrows \pm^1/_2) \simeq 3/2/1$ for small η; bismuth-209, $\nu(\pm^9/_2 \rightleftarrows \pm^7/_2)/\nu(\pm^7/_2 \rightleftarrows \pm^5/_2)/\nu(\pm^5/_2 \rightleftarrows \pm^3/_2)/\nu(^3/_2 \rightleftarrows \pm^1/_2) \simeq 4/3/2/1$ for small η.

Results and Discussion

Nqr spectroscopy measures the coupling between the nuclear electric quadrupole moment, Q, and the electric field gradient, q, in a crystalline lattice. Arsenic, chlorine, and bromine have nuclear spins of $^3/_2$ and only the nuclear quadrupole coupling constant, e^2Qq/h, can be measured to a fair approximation from the powder spectrum. Antimony-121 has $I = {}^5/_2$, antimony-123 has $I = {}^7/_2$, and bismuth-209 has $I = {}^9/_2$ nuclear spin so that for these nuclei both e^2Qq/h and the electric field gradient asymmetry parameter, η, can be determined directly from the spectrum. The point groups D_{3h} and C_{3v} will not generate asymmetry in the central atom or apical atom electric field gradients.

Electronic Inductive Effects.—Large shifts in the ^{75}As resonance frequencies are observed in R_3AsX_2 compounds as R and X are varied. In Table I, the ^{75}As frequency shifts 18–20 MHz as R is changed from the phenyl to the methyl group. On the other hand, the ^{75}As frequency changes by only about 7 MHz as X is changed from fluorine to bromine. In a qualitative sense, then, the contribution of the equatorial groups to the electronic structure of the arsenic atom appears to be considerably greater than that of the apical groups.

The relative nucleophilic character of the methyl, benzyl, and phenyl groups can be inferred from the relative strengths of propionic acid ($K = 1.34 \times 10^{-5}$), β-phenylpropionic acid ($K = 4.25 \times 10^{-5}$), and phenylacetic acid ($K = 5.27 \times 10^{-5}$). It is more reasonable to consider these acids rather than acetic, benzoic, and phenylacetic acids since, in the latter, both resonance and inductive effects will be important in determining the acid strengths. The nucleophilicity of the groups decreases according to $CH_3 > C_6H_5CH_2 > C_6H_5$ by this criterion. Examination of the ^{75}As data in Table I reveals that for a given halogen $\nu(^{75}As–CH_3) > \nu(^{75}As–CH_2C_6H_5) > \nu(^{75}As–C_6H_5)$. Figure 2 demonstrates that the correlation between $\nu(^{75}As–R)$ and the acid strengths of $R–CH_2COOH$ is qualitatively good but not quantitative. This is almost certainly a result of differences in crystal lattice effects and the fact that

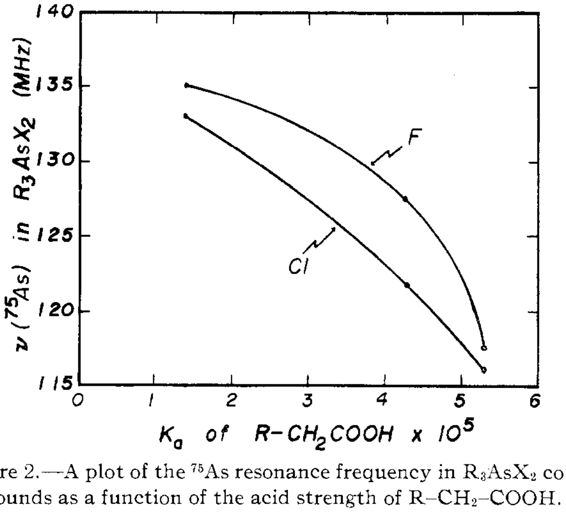

Figure 2.—A plot of the ^{75}As resonance frequency in R_3AsX_2 compounds as a function of the acid strength of $R–CH_2–COOH$.

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[17] T. P. Das and E. L. Hahn, *Solid State Phys., Suppl.*, **1**, 13 (1958).

the three groups are sterically quite different. Consideration of the general nature of these trends leads to some qualitative information about the electronic structure of the arsenic atom.

In valence bond notation, the trigonal-bipyramidal geometry about the arsenic atom may be attained by forming $4s4p^34d_{z^2}$ hybrid orbitals. It is well known that d orbitals contribute much less to the electric field gradient at a nucleus than do p orbitals[17] so that the reasoning may be simplified without significant loss in generality to a discussion of p orbitals. The s orbital, being spherically symmetric, contributes nothing directly to the nqr effect. The atomic electric field gradient, q_{at}, is related to the molecular value, q_{mol}, according to[17]

$$q_{\text{mol}} = q_{\text{at}}\left[N_{p_z} - \frac{N_{p_x} + N_{p_y}}{2}\right] \qquad (1)$$

where N_{p_x}, N_{p_y}, and N_{p_z} are the orbital populations of the p_x, p_y, and p_z atomic orbitals. This equation presumes that the Z principal axis of the electric field gradient is coincident with the p_z orbital (see Figure 1). q_{at} is unknown for arsenic, antimony, and bismuth so it is necessary to consider relative effects rather than absolute ones. Arsenic–halogen σ bonding manifests itself in the arsenic and halogen p_z orbitals. Arsenic–carbon σ bonding uses the p_x and p_y orbitals on the arsenic atom. According to the acid strength criterion, as R becomes more electron releasing in R_3AsX_2, the arsenic resonance frequency increases. The bracketed quantity in (1) must, therefore, be negative because N_{p_x} and N_{p_y} will increase as R becomes progressively more nucleophilic. If the quantity is negative, one could anticipate that placing more nucleophilic atoms at the apical positions of the trigonal bipyramid should decrease the ^{75}As frequency by increasing N_{p_z}. This is precisely what is observed in going from fluorine to chlorine to bromine. The fact that the quantity is negative supports the initial contention of this section that the As–R interaction is more important to the electronic structure of the As(V) atom than the As–X interaction.

The halogen atoms, although more or less covalently bound to the arsenic atom, have considerable ionic character. For example, the chlorine resonance frequencies in the R_3AsCl_2 compounds are in the range of those found[18] in $SnCl_6^{2-}$ and $PbCl_6^{2-}$. A similar argument as given above can be made for the chlorine orbital populations using eq 1. The bracketed quantity will be negative for the halogens because the p_x and p_y orbitals of chlorine are filled. In the series $(CH_3)_3AsCl_2$, $(C_6H_5CH_2)_3AsCl_2$, and $(C_6H_5)_3AsCl_2$ the ^{35}Cl frequency increases. Since the nucleophilicity of the equatorial group decreases along the same series, the population of the arsenic p_z orbital, which is involved in the As–Cl bond, decreases slightly. In turn, the chlorine p_z orbital population decreases to fill the void somewhat and results in the observed increase in the ^{35}Cl frequencies.

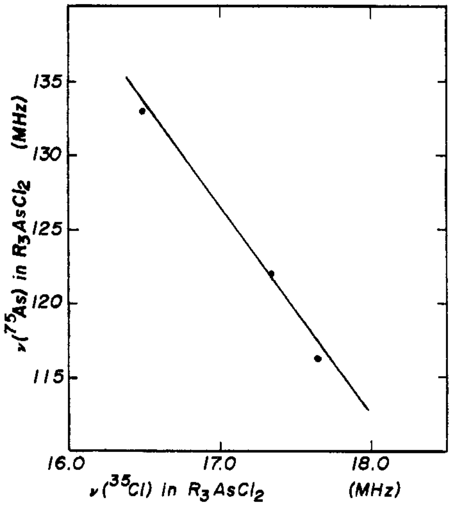

Figure 3.—A plot of ^{75}As resonance frequencies *vs.* ^{35}Cl frequencies in R_3AsCl_2 compounds.

Figure 3 demonstrates the fact that the amount of electron density released into the arsenic atom by the R group shows up in nearly direct proportion in the ^{35}Cl p_z orbital. Qualitatively, this indicates that eq 1 is a good representation of the orbital contributions to the electric field gradient in these compounds.

The above observation may be compared to those in the trivalent As(III) compounds. The crystal structure of triphenylarsine is complicated and has not been solved.[19] Tri-*p*-tolylarsine, however, has a flattened pyramidal structure with C_3 molecular symmetry in which the arsenic atom sits at the apex of a pyramid.[20] It is reasonable to assume from this and by analogy to the corresponding antimony[21] compounds that other tricoordinate arsines have this geometry as well. The Z principal axis of the electric field gradient will lie near the threefold axis of these systems (p_z orbital). Table I shows that the trend in the arsenic(III) resonance frequency is $(C_6H_5)_3As > (C_6H_5CH_2)_3As$ which is opposite that of the arsenic(V) data. The bracketed quantity in (1) is apparently positive in the R_3As compounds because N_{p_x} and N_{p_y} will increase in going from the phenyl to the benzyl group. For this to happen, the extra two electrons in As(III) compared to As(V) must be predominantly p in character. This fact helps to explain why R_3As molecules are intermediate between pyramidal and planar. If the orbital were purely p in character, the molecule would be planar; if it were purely s, R_3As would be pyramidal. The M(V) resonance frequencies are observed to be greater in all cases than the M(III) frequencies so that the population difference between the p_z orbital and the p_x and p_y orbitals must be less in M(III) than in M(V).

Hydrogen–deuterium isotope effects in nqr spectroscopy have recently been analyzed[22] for $(CH_3)_3SbX_2$ and $(CD_3)_3SbX_2$ (X = Cl and Br). The trends in the ^{75}As and ^{35}Cl resonances in tribenzylarsenic dichloride and

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[18] D. Nakamura, *Bull. Chem. Soc. Jap.*, **36**, 1162 (1963).

[19] J. Trotter, *Can. J. Chem.*, **40**, 1878 (1962).

[20] J. Trotter, *ibid.*, **41**, 14 (1963).

[21] I. G. M. Campbell, *J. Chem. Soc.*, 3116 (1955).

[22] T. B. Brill and Z Z. Hugus, Jr., *J. Chem. Phys.*, in press.

tribenzylarsenic dichloride-d_2 are completely consistent with the previous conclusions.

The data for antimony and bismuth in Tables II and III concur with the interpretations given above for arsenic. Although the trends for the R_3SbX_2 compounds are the same as those in the R_3AsX_2 series, they are not as well defined. The sources of the variation in the electric field gradient are in the outer electron shells of these atoms so that an increase in the atom size should somewhat decrease the extent to which the effects can be observed.

The decrease in bromine resonances in the compounds $(C_6H_5)_3MBr_2$, where M = As, Sb, and Bi, reflect the increase in metallic character of M. The M–Br bond becomes more ionic going down in the series of congeners because the bromine atom can extract, through its p_z orbital, an increasing amount of electron density from the metal to which it is bonded. According to eq 1 an increase in p_z orbital population for a halogen will decrease its electric field gradient in a molecule.

Structural Implications.—In most cases, a single set of halogen and group Va atom resonance frequencies was observed in the compounds studied. This result indicates that a single crystallographic site exists for these atoms in the unit cell. Triphenylarsine has two ^{75}As resonances at 77°K and more at room temperature.[4a] Two Sb sites in $(C_6H_5)_3Sb$ were found both at 77°K and at room temperature.[4b] Two bismuth sites were also found in $(C_6H_5)_3BiX_2$.

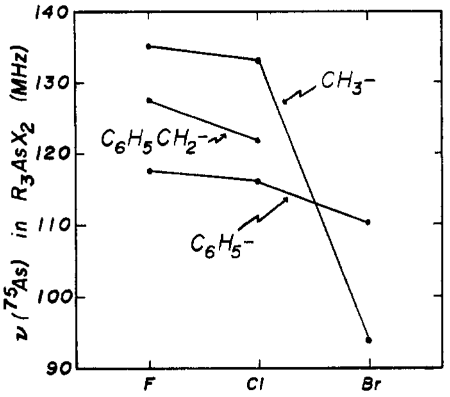

Figure 4.—A plot of the ^{75}As resonance frequencies in R_3AsX_2 compounds as a function of X.

In Figure 4, a plot has been made of the ^{75}As resonance frequencies in the fluorine, chlorine, and bromine compounds to demonstrate a possible structural irregularity. The $(C_6H_5)_3AsX_2$ compounds form a progression that leads one to predict that the fluorine, chlorine, and bromine moieties are isostructural. The ir spectrum of $(C_6H_5)_3AsF_2$ is completely consistent with the trigonal-bipyramidal geometry.[12] On the basis of this and the nqr data the chlorine and bromine analogs appear to have trigonal-bipyramidal structures. On the other hand, the $(CH_3)_3AsX_2$ compounds do not form a similar progression. Trimethylarsenic difluoride and trimethylarsenic dichloride appear to behave like the phenyl compounds but the bromide is considerably different. $(CH_3)_3AsF_2$ and $(CH_3)_3AsCl_2$ probably have D_{3h} symmetry based on ir data.[12] It is not possible to determine the new geometry of $(CH_3)_3AsBr_2$ from the nqr spectrum alone but a shift to pseudotetrahedral C_{3v} symmetry as $(CH_3)_3AsBr^+$ is not inconsistent with the results. The ^{75}As frequency might be expected to be somewhat lower with C_{3v} symmetry than in a similar molecule with D_{3h} symmetry. Tribenzylarsenic difluoride and dichloride show characteristics expected of them if they had the trigonal-bipyramidal configuration. The preparation of the bromide analog has not been reported to date.

A perplexing problem arises as to why $(CH_3)_3AsBr_2$ prefers to become saltlike as $(CH_3)_3AsBr^+Br^-$ in the solid state whereas $(C_6H_5)_3AsBr_2$ remains as a trigonal bipyramid. If steric effects alone were important, then the presence of $(C_6H_5)_3AsBr_2$ could not be explained in the light of $(CH_3)_3AsBr^+Br^-$. More likely, the interplay of intramolecular steric and electronic effects and crystal lattice stabilization effects is important in determining the geometry assumed. The nucleophilicity of the methyl groups may have the effect of stabilizing the high formal charge on arsenic such that only a single bromine atom is needed to attain an energetically favorable coordination number about the arsenic atom. The phenyl compound with less nucleophilic equatorial groups may necessitate a higher arsenic coordination number in order to lower the arsenic formal charge. The bulky nature of the phenyl and benzyl groups may contribute a lattice stabilization of the five-coordination as well. It should be noted that in ionizing media, such as acetonitrile, $(C_6H_5)_3AsCl_2$ and $(C_6H_5)_3AsBr_2$ conduct weakly due to the presence of $(C_6H_5)_3AsX^+$ and X^- ions.[23] In any case, these arsenic compounds apparently lie near the borderline between four- and five-coordination in the periodic table.

The asymmetry parameter, η, is an additional quantity which can be used in structural arguments for the antimony and bismuth molecules. As pointed out before, D_{3h} and C_{3v} symmetries require $\eta = 0$ at the antimony and bismuth nuclei. Several crystal structure determinations have been carried out on these compounds, but all are complicated by heavy-metal scattering. A specific distortion of one of the phenyl rings out of the equatorial plane in $(C_6H_5)_3SbCl_2$ was noted by Polynova and Porai-Koshits.[8] Hawley and Ferguson[14] found that in $(C_6H_5)_3BiCl_2$ one of the phenyl rings is twisted so that the "propellor" arrangement of phenyl rings about the Cl–Bi–Cl axis is disturbed. Because a perfect threefold axis does not exist in these compounds, a small value of η would be expected. In addition, the crystal lattice undoubtedly generates some electric field gradient asymmetry. However in all compounds studied, only small values of η were observed, and, in addition, no abnormality in the resonance frequency trends was observed. The molecular symmetry of the benzyl compounds and tri-

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(23) G. S. Harris, *Proc. Chem. Soc., London*, 65 (1961).

phenylantimony difluoride and dibromide is then almost surely similar to that of $(C_6H_5)_3SbCl_2$. The apparent lack of a large value for η in the benzyl compounds places a restriction on the arrangement which the R groups can assume. The threefold X–M–X axis cannot be appreciably disturbed.

Two crystallographically different sites for bismuth in $(C_6H_5)_3BiCl_2$ are evident from the nqr data. In agreement with this, Hawley and Ferguson[14] found that there are two molecular groups in the asymmetric unit of the crystallographic cell. Our nqr data indicate that $(C_6H_5)_3BiBr_2$ is probably isostructural with $(C_6H_5)_3BiCl_2$. Three bromine sites apparently exist in $(C_6H_5)_3BiBr_2$ giving the resonance frequency intensity ratios of 2:1:1. The Bi–Cl bond lengths in one molecule of $(C_6H_5)_3BiCl_2$ were found[14] to be 2.615 and 2.530 Å while in the other molecule they were much less different, 2.579 and 2.560 Å. A similar situation might exist in the bromine compound. The chlorine resonances in $(C_6H_5)_3BiCl_2$ were too weak to be observed.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF GEORGIA, ATHENS, GEORGIA 30601

Isolation of Pure Mixed μ_4-Oxo-hexa-μ-carboxylato-tetraberyllium Compounds of the General Formula $Be_4O(CH_3CO_2)_x(CCl_3CO_2)_{6-x}$[1]

BY KENNETH J. WYNNE AND W. BAUDER

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The mixed μ_4-oxo-μ-hexacarboxylato-tetraberyllium derivatives $Be_4O(CH_3CO_2)_5(CCl_3CO_2)$, $Be_4O(CH_3CO_2)_3(CCl_3CO_2)_3$, and $Be_4O(CH_3CO_2)(CCl_3CO_2)_5$ have been prepared by fractional crystallization from equilibrated chloroform solutions of $Be_4O(CH_3CO_2)_6$ and $Be_4O(CCl_3CO_2)_6$. The mass and proton nuclear magnetic resonance spectra were important in providing evidence for the existence of pure compounds. A study of the proton nmr spectrum *vs.* time on solutions of the mixed carboxylates indicated carboxylate scrambling occurred with increasing rate in the order $Be_4O(CH_3CO_2)_5(CCl_3CO_2) < Be_4O(CH_3CO_2)_3(CCl_3CO_2)_3 < Be_4O(CH_3CO_2)(CCl_3CO_2)_5$. It is postulated that carboxylate scrambling occurs *via* the ionic dissociative process $Be_4O(RCO_2)_x(R'CO_2)_{6-x} \rightarrow Be_4O(RCO_2)_x(R'CO_2)_{5-x}^+ + R'CO_2^-$.

A number of investigators have claimed the preparation of mixed μ_4-oxo-hexa-μ-carboxylato-tetraberyllium species.[2] However Marvel[3a] and Hardt[3b] have demonstrated that the "compounds" were actually mixtures of mixed carboxylates of the general formula $Be_4O(RCO_2)_x(R'CO_2)_{6-x}$, where $0 < x < 6$.

Isolation of pure mixed carboxylates seemed desirable for several reasons. We were interested in determining qualitatively the rate of carboxylate scrambling in a mixed species. The mechanism of the exchange process as well as the relative donor abilities of differing carboxylate ligands was also of interest. We sought to isolate a mixed compound in which the carboxylate groups would differ appreciably in base strength and molecular weight and found the trichloroacetate–acetate system fit these requirements. We have communicated the findings of our initial study,[4] the complete results of which are reported below.

Experimental Section

The usual precautions for working with beryllium compounds were observed.[5] Generally, operations were carried out in nitrogen-filled polyethylene bags regardless of whether the material being worked with was hygroscopic. This approach helped limit beryllium contamination in the laboratory. Mass spectra were obtained using a Perkin-Elmer Hitachi RMU-6E mass spectrometer. Proton nmr spectra were obtained by means of a Varian HA 100 nuclear magnetic resonance spectrometer. Chemical shifts are reported *vs.* internal tetramethylsilane reference.

μ_4-Oxo-hexa-μ-acetato-tetraberyllium was prepared by refluxing beryllium oxide in a twofold excess of acetic acid and purified as previously reported.[6]

Beryllium Trichloroacetate Dihydrate.—The preparation of this compound was similar to the method of Parsons and Sargent,[7] although we used $Be(OH)_2$ in place of $BeCO_3$. *Anal.* Calcd for $C_4H_4BeCl_6O_6$: C, 12.99; H, 1.09; Cl, 57.52. Found: C, 12.98; H, 1.38; Cl, 56.47.

Decomposition of $Be(CCl_3CO_2)_2 \cdot 2H_2O$ in a sealed capillary began at 100° with further observations being dependent on the rate of heating. If the sample was heated slowly (2°/min), quiet evolution of vapor was observed up to the melting point (270°) where vigorous bubbling occurred. The liquid appeared stable to 300°. When the sample was cooled and reheated some of the sample melted at 210°. However, if the sample temperature was initially raised rapidly (50°/min) melting and bubbling took place at 160–175° followed by solidification. After this, observations at higher temperatures were identical with the

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[1] Paper presented at the 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969.

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