Table I. Epr Data for $ClOCl^+$, $FClO^+$, OClO, and Related Radicals

Radical	⟨g⟩	a_{17}, G	a_{19}, G	a_{35}, G	Ref
$ClOCl^+$	1.9986[a]	20.6[b]		2.25 (2)	*c*
$FClO^+$	2.0059	18.0	20.4	12.9	*c*
OClO	2.0100	11.5 (2)		17.9	*c*
FOO	2.0038	14.5	12.8		*d*
		22.2			
F_3COOO	2.0037	3.6	6.75		*e*
		14.0	0.55 (2)		
		23.3			
OOO^-	2.0096	10.5 (2)			*f*
		22.2			
$(H_3C)_3COO$	2.0146	23.4			*g*
		17.6			

[a] ±0.0002. [b] ±0.10 G. [c] This work. [d] Reference 6. [e] Reference 7. [f] S. Schlick, *J. Chem. Phys.*, 56, 654 (1972). [g] J. A. Howard, *Can. J. Chem.*, 50, 1981 (1972); K. Adamic, K. U. Ingold, and J. R. Morton, *J. Amer. Chem. Soc.*, 92, 922 (1970).

in O_3^-, we would therefore expect the hyperfine interaction of the terminal oxygen nucleus of FOO to be considerably larger than 10.5 G and that of its central oxygen to be rather smaller than 22.2 G, these being the respective isotropic interactions in O_3^- itself.[8] We therefore conclude that in FOO the larger (22.2 G) interaction is to be associated with the terminal oxygen nucleus, and the smaller (14.5 G) interaction is to be associated with the central oxygen. By analogy with FOO we conclude that in $F_3CO'''O''O'$ $a'_{17} = 23.3$ G, $a''_{17} = 14.0$ G, and $a'''_{17} = 3.6$ G.

A similar conclusion, later confirmed by Howard,[9] was reached by Adamic, *et al.*,[10] on the basis of line width variation across the ^{17}O hyperfine manifolds of the peroxy radical $(H_3C)_3COO$.

Experimental Section

The solvent, ClF_3 (Matheson), was handled in a copper vacuum line fitted with Whitey valves, Type 1VF4. The epr sample tubes were either Teflon FEP or Suprasil, 4-mm o.d. Arsenic pentafluoride (Allied Chemical) was used as a Lewis acid, and the ^{17}O source was water containing approximately 25 atom % ^{17}O (Yeda). In order to eliminate all traces of atmospheric moisture the entire vacuum system and the sample tubes were exposed to 0.5 atm of ClF_3 vapor for 0.5 hr. After reevacuation of the system approximately 50 μmol of AsF_5 and 10 μmol of enriched H_2O were dissolved in excess (approximately 200 μl) ClF_3. The samples could be photolyzed with a 1000-W Schoeffel Hg-Xe lamp; epr spectra were obtained with a Varian E-12 spectrometer equipped with a variable-temperature accessory. A CMC 707B frequency counter was used in conjunction with an HP540B transfer oscillator and Varian F-8A fluxmeter to measure the microwave frequency and magnetic field, respectively.

We found that if a sample of ClF_3 containing dissolved AsF_5 and water was photolyzed at −70°, a powerful signal due to $ClOCl^+$ could be detected. This signal disappeared rapidly on extinguishing the light. Use of water enriched in ^{17}O enabled us to determine a_{17} for this radical (20.6 G). The signal due to $FClO^+$ persisted for many hours after extinguishing the light and appeared to be optimized from the point of view of resolution of its hyperfine structure at −30°. Again, with the aid of ^{17}O-enriched water we were able to determine its a_{17} (18.0 G).

It may also be noteworthy that the epr spectrum of OClO appeared (without photolysis) in samples of ClF_3-AsF_5 to which several 10-μmol aliquots of water had been added. The ^{17}O hyperfine interaction was found to be 11.5 G, in excellent agreement with the value reported recently for OClO in toluene.[11]

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Registry No. $ClOCl^+$, 51174-96-0; $FClO^+$, 51174-97-1; OClO, 10049-04-4; ^{17}O, 13968-48-4.

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Mossbauer Effect in Oxygen-Bonded Antimony(III) Compounds. Aliphatic Esters and Oxobis(diphenylantimony)

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The effect of a group on the Mossbauer spectrum of a central metallic element can best be seen in a series of compounds with similar geometry. The ^{121}Sb Mossbauer effect has been studied in trivalent Sb(III) bonded to oxygen[2,3] and to carbon,[4,5] as well as other atoms. The several modifications of Sb_2O_3 are the only ones studied to date in the first category, as other inorganic oxides have more than three Sb-O bonds.[2b,3] In the present work we report results on a series of $Sb(OR)_3$ compounds, where R is an aliphatic group. The compound $[(C_6H_5)_2Sb]_2O$, oxobis[diphenylantimony(III)], which has both Sb-O and Sb-C bonds in the same molecule, has also been studied. Evidence that a Gol'danskii-Karyagin effect[6] does not occur in these compounds at 4°K has been obtained.

Experimental Section

Preparation and characterization of the $Sb(OR)_3$ compounds have been described elsewhere.[7] Because these are unstable when exposed to moist air, they were handled in a dry nitrogen atmosphere. Just prior to use, they were analyzed for Sb and agreement within at least 0.6 absolute per cent of the calculated percentage was taken as a criterion for lack of decomposition. The $[(C_6H_5)_2Sb]_2O$ was obtained from M & T Chemicals, Inc., Rahway, N. J., and was pure according to chemical analysis. *Anal.* Calcd for $[(C_6H_5)_2Sb]_2O$: Sb, 42.88; C, 50.7; H, 3.55. Found: Sb, 43.04; C, 50.2; H, 3.49.

The Mossbauer spectra were taken at liquid helium temperature as described earlier.[5] The $Sb(OR)_3$ compounds studied are liquids at room temperature, so absorbers were prepared by pouring the liquid onto polyethylene powder, quick-freezing in liquid nitrogen, and keeping the sealed holder cold until insertion into the cryostat. Because of the difficulty in handling these samples, the sample thickness has more error than for the $[(C_6H_5)_2Sb]_2O$ sample, a stable solid at room temperature.

Analysis of the spectra followed the procedure of Shenoy and Dunlap[8] with modifications to search for a Gol'danskii-Karyagin effect.[9] In the case of compounds with $\eta \approx 0$ this means allowing the $\Delta m = 1$ and $\Delta m = 0$ transition intensities to vary independently. For large η, m is no longer a valid quantum number. The ratio R_2/R_1,[9] corresponding to the intensity ratio $\Delta m = 0$ to $\Delta m = 1$ for $\eta = 0$, can still be determined. It proved unnecessary to invoke further

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Table I. Mossbauer Parameters at 4°K

Compd	mg of Sb/cm^2	Intensity,[a] %	R_2/R_1[a] (±0.05)	Width[b] (±0.1)	IS[b] (±0.1)	e^2qQ[b] (±0.5)	η[c]
$Sb(OC_2H_5)_3$	10	27	1.26	2.5	−3.3	19.5	
$Sb(OC_3H_7)_3$	14	38	1.34	2.6	−3.4	19.9	
$Sb(OC_4H_9)_3$	10	34	1.29	2.6	−3.2	19.0	
	5	23	1.24	2.6	−3.5	19.3	
$Sb[OC(CH_3)_3]_3$	10	27	1.27	2.5	−2.8	19.1	
	6	24	1.16	2.7	−3.0	18.7	
$[(C_6H_5)_2Sb]_2O$	15.0	34	1.05	2.7	−1.2	21.0	0.89 ± 0.05
	10.0	26	1.01	2.8	−1.1	20.8	0.89 ± 0.05
	6.8	18	1.04	2.6	−1.0	19.9	0.86 ± 0.05
	3.8	11	0.98	2.8	−1.0	20.0	0.95 ± 0.10

[a] The intensity quoted is for $\Delta m = 1$. The ratio R_2/R_1[9] is the intensity ratio $\Delta m = 0$ to $\Delta m = 1$. [b] Units are mm/sec. Line width is at half-maximum. Isomer shifts (IS) are given relative to InSb. [c] The expected value of $\eta \approx 0.1$[7] for the $Sb(OR)_3$ compounds does not measurably affect the Mossbauer spectrum.

parameters for analyzing these spectra. The data are summarized in Table I. The two types of compounds have quite different and characteristic spectra, as seen in Figure 1.

Results and Discussion

The $Sb(OR)_3$ compounds gave positive values for the quadrupole coupling constant, indicative of the excess p-electron density in the lone-pair orbital. The values of e^2qQ in Table I are probably slightly high, as the Mossbauer spectral analysis for ^{121}Sb has a tendency to overestimate e^2qQ.[5] Measurement by nqr on the similar $Sb[OCH(CH_3)_2]_3$ gave, at 77°K, $e^2qQ = 560.6$ MHz (18.6 mm/sec) and $\eta = 0.138$.[7,10] Values of η in the range 0.1–0.2 did not change the fit of the Mossbauer spectra to any measurable degree, and it can be presumed η is no greater than this, noting the approximately threefold symmetry axis at Sb. The values of e^2qQ are somewhat larger than those determined for Sb_2O_3, 18.2 mm/sec,[3] and $(CH_3)_3Sb$, 16.3 mm/sec.[5]

The fact that both e^2qQ and IS values are essentially constant for these compounds is in accord with the previous conclusion that no significant electronic transmission effects occur from R through oxygen.[7] The bulky $C(CH_3)_3$ group does give a less negative isomer shift or slightly lower s-electron density at Sb. The ir and Raman spectra of this compound have been interpreted as indicating increased s character in the σ-bonding orbitals,[7] which would account for a lowered s density at Sb. It is of particular interest to note the isomer shift values of $Sb(OR)_3$ are essentially the same as that for Sb_2O_3 (−3.3 mm/sec) but appreciably different from antimony(III) oxides containing more than three Sb–O bonds (−6.3 mm/sec for Sb(III) in Sb_2O_4).[3]

In compounds of the type $(C_6H_5)_2Sb(CH_2)_nSb(C_6H_5)_2$ an improvement in fit was observed when the $\Delta m = 0$ and $\Delta m = 1$ intensities were allowed to vary independently.[5,11] This same effect was noted in the $Sb(OR)_3$ esters. Being quick-frozen on polyethylene powder and mixed, they are unlikely to have preferred orientation in the absorber. In order to eliminate possible saturation effects, the R_2/R_1 ratios (Table I) need to be extrapolated to zero thickness. If R_2/R_1 differs from unity at zero thickness, it is likely due to anisotropy in the mean-square vibrational amplitude of the Mossbauer nucleus (the Gol'danskii-Karyagin effect[6]). The need for measuring R_2/R_1 as a function of thickness is apparent, as measurements at 10 mg of Sb/cm^2 would appear to indicate appreciable vibrational anisotropy. Extrapolating the $Sb(OR)_3$ data as a group, R_2/R_1 is 1.1, but the precision is such that 1.0 is also possible. In any event the vibrations are fairly isotropic, with $a = k^2 [\langle z^2 \rangle - {}^1/_2(\langle x^2 \rangle + \langle y^2 \rangle)]^9$ between 0 and 1.

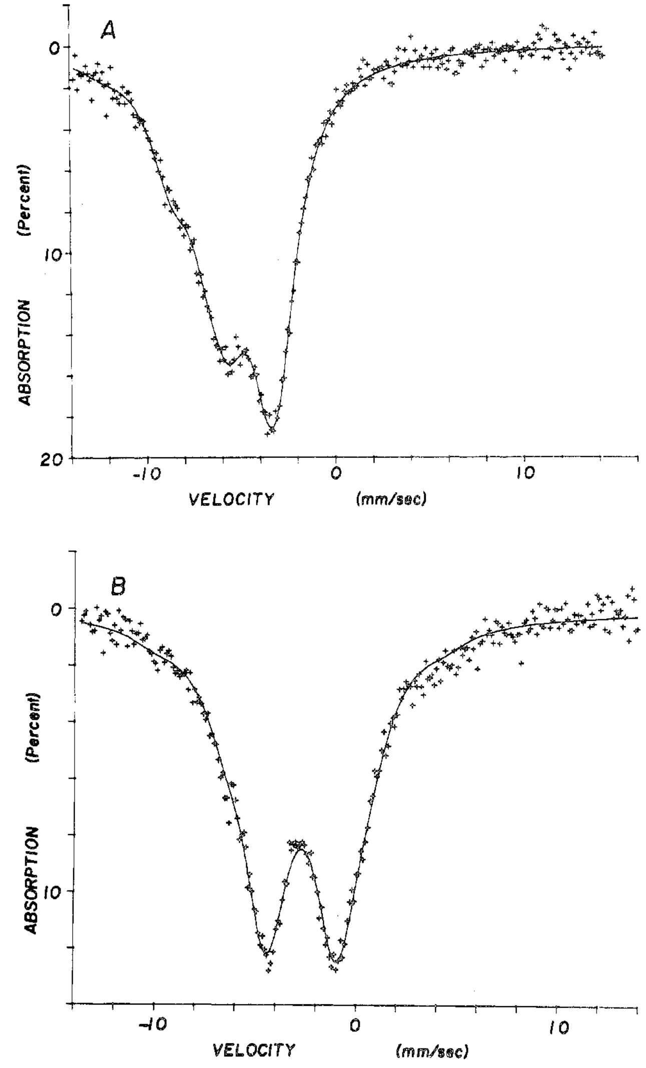

Figure 1. Mossbauer spectra of typical samples, with computer fit to the data. The parameters in the fit are those listed in Table I, except that the isomer shifts are shown as measured with the $Ni_{21}Sn_2B_6$(^{121}Sb) source 1.68 mm/sec more negative than InSb:[5] (A) $Sb(OC_4H_9)_3$, 10 mg of Sb/cm^2; (B) $[(C_6H_5)_2Sb]_2O$, 10 mg of Sb/cm^2. The distinctive appearance of spectrum B is explained by the large $\eta = 0.89$.

The Mossbauer spectrum of $[(C_6H_5)_2Sb]_2O$ is quite distinctive (Figure 1) and was first considered to consist of two peaks. However, these gave unrealistic isomer shifts, one more negative than that for Sb_2O_3 and the other more posi-

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(11) A misprint in ref 5 labels both intensities as $\Delta m = 0$. Similar to the present compounds, the $\Delta m = 1$ has the smaller intensity and $R_2/R_1 > 1$.

tive than that for $(C_6H_5)_3Sb$. An alternative fit which gave smaller χ^2 with fewer parameters is obtained from one site with a large η. The ^{121}Sb spectrum becomes more symmetrical as $\eta \rightarrow 1$,[12] and indeed we obtained good fits to a series of absorbers (Table I) with $\eta = 0.90 \pm 0.05$. Although nonzero η did improve the fit for orthorhombic Sb_2O_3,[2a] this present case is the first in which a large value of η has resulted in a resolved splitting in the ^{121}Sb Mossbauer spectrum.[13] Independent confirmation of the large value of η was sought by nqr measurements, but signals were not observed. Although the fit to two peaks would require radically different Sb sites, which we felt unlikely, it was desirable to eliminate this possibility, and hence the crystal structure of the compound was determined.[14] The molecule has two very similar Sb sites, each bonded to two carbons at ~2.15 Å (~95° bond angle) and connected by a bridging oxygen at ~1.96 Å (SbOSb angle 122°). The CSbO angles vary, one being smaller (92-93°) than the other (95-97°). Since $\eta = (V_{xx} - V_{yy})/V_{zz}$, and thus measures the deviation from axial symmetry in the field gradient, the fact that one of the three bonds to Sb is different could presumably account for the large η. Two other compounds of Sb(III), at least, have appreciable η. By nqr, Semin, *et al.*,[15] measured $\eta = 0.825$ for $(C_6H_5)_2SbCl$ and 0.499 for $(C_6H_5)_2SbC{\equiv}CSb(C_6H_5)_2$. The similarity of these compounds to $(C_6H_5)_2SbOSb(C_6H_5)_2$ is clear. It is noted that $(C_6H_5)_2Sb(CH_2)_nSb(C_6H_5)_2$ compounds have $\eta \approx 0$.[5] Thus, the appearance of large η in R_2SbX seems to require excess p-electron density on X, in the form of unshared lone pairs or an acetylene linkage.[16] Whether the interaction producing the asymmetric field gradient is primarily π or σ remains uncertain,[5] because η is also extremely sensitive to small angular distortions in the molecule according to the point charge model.[17] The largest η is, however, produced by the most electronegative X, oxygen.

The value of e^2qQ for the oxobis[diphenylantimony(III)] is about the same as those for the $Sb(OR)_3$ esters (Table I) and larger than for $(C_6H_5)_3Sb$ and other Sb-C bonded compounds.[5] The *z* axis of the field gradient must still be in the general direction of the lone pair, as any appreciable shift toward the Sb-O bond would decrease the p_z electron excess and thus the magnitude of e^2qQ. The isomer shift (Table I) is between those for the $Sb(OR)_3$ compounds (and Sb_2O_3) and that for $(C_6H_5)_3Sb$. If one takes the extrapolated value of IS for SbX_3 compounds at zero ionicity (−8.5 ± 0.5 mm/sec)[18] as the zero point, one can predict IS for the oxobis(diphenylantimony) using the concept of partial isomer shifts,[19] here applied for the first time to Sb(III) compounds. We obtain the shift for Sb-O-Sb from Sb_2O_3[3] as $(1/3)\cdot(-3.3 + 8.5) = 1.7$ mm/sec and for an Sb-(C_6H_5) bond from $(C_6H_5)_3Sb$[5] as $(1/3)(-0.6 + 8.5) = 2.6$ mm/sec. The predicted shift for the $[(C_6H_5)_2Sb]_2O$ is $IS = -8.5 + 1.7 + 2(2.6) = -1.6 \pm 0.5$ mm/sec, in reasonable agreement with that measured.

The spectra are distinct enough that deviations in intensities of the various lines should be apparent. However, within experimental error the ratio R_2/R_1 is unity, even for relatively thick samples. Thus, in spite of the appreciable asymmetry in the field gradient, the vibrational amplitude is quite isotropic. In the X-ray structure determination,[14] the Sb atom had markedly anisotropic thermal parameters at room temperature. Thus, the low temperature of the Mossbauer measurements not only reduces the vibrational amplitude but also makes it more symmetric. The lack of a Gol'danskii-Karyagin effect in $[(C_6H_5)_2Sb]_2O$ at 4°K, when vibrational asymmetry is so apparent at room temperature, indicates only very unusual cases will have this effect at the typical temperature of ^{121}Sb Mossbauer measurements.[20]

In conclusion, the present studies provide further evidence that in a given geometry, the atoms bound directly to Sb are the primary influence on the observed Mossbauer parameters for ^{121}Sb. In R_2SbX compounds, X groups with nonbonded p electrons produce appreciable asymmetry in the field gradient at Sb, but little asymmetry in the vibrational ellipsoid is observed at 4°K.

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Registry No. $Sb(OC_2H_5)_3$, 10433-06-4; $Sb(OC_3H_7)_3$, 4292-34-6; $Sb(OC_4H_9)_3$, 2155-74-0; $Sb[OC(CH_3)_3]_3$, 10433-03-1; $[(C_6H_5)_2Sb]_2O$, 7065-22-7; ^{121}Sb, 14265-72-6.

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