Contribution from the Department of Chemistry,
North Carolina State University, Raleigh, North Carolina 27607

Antimony(V) Orbital Populations from Antimony-121 Mössbauer Data

L. H. BOWEN* and G. G. LONG

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A method is presented which utilizes both Mössbauer isomer shifts and quadrupole coupling constants to obtain the electron populations in the hybrid atomic orbitals used by antimony(V) to form bonds. Here, it is applied to series of compounds in which the antimony is bonded to phenyl and/or Cl groups (included are new Mössbauer data for seven compounds as well as previously reported data), but the method should have general applicability. Comparisons are made with halogen NQR results and with Sn(IV) Mössbauer data. The electron population along the Sb–R bond, σ_R (R being phenyl or methyl), tends to increase as the number of electronegative groups attached to Sb increases. The 5s character of the apical bonds in R_3SbX_2 and R_4SbX compounds is appreciable but varies only slightly among compounds. Evidence is presented that bridging chlorines produce a somewhat larger σ_{Cl} and smaller value of $\langle r^{-3}\rangle_p$ than nonbridging.

Introduction

For pentacoordinate organoantimony compounds of the type R_3SbX_2 and R_4SbX (R = phenyl (Ph), methyl (Me)), Sams and coworkers[1,2] have shown that the quadrupole splitting data from ^{121}Sb Mössbauer spectroscopy can be interpreted in terms of an additive model. Using the formalism developed primarily for Sn(IV) compounds,[3] they have reported a number of ligand partial field gradients (PFG) for R and X groups in the trigonal-bipyramidal geometry. Unlike the ^{119}Sn case, the sign of e^2qQ is easily obtained from the ^{121}Sb Mössbauer spectrum, which assists in the interpretation. Using two octahedral diphenyl complexes, Ruddick and Sams[4] have also verified that cis and trans isomers of Sb(V) have e^2qQ in the ratio −1:2, as predicted by the additive model. Thus it seems clear that for organoantimony compounds, in these two geometries at least, the field gradient is approximately additive. This fact should prove useful in future studies of compounds with unknown structure.

However, for the other main parameter from the ^{121}Sb Mössbauer spectrum, the isomer shift (δ), interpretations have been more qualitative. Linear correlations have been found between δ and e^2qQ for Ph_3SbX_2[1] and Me_3SbX_2,[2] while Ph_4SbX does not give such a correlation.[1] However, both Ph_3SbX_2 and Ph_4SbX give linear correlations of δ with the Sb–X bond ionicity.[5] Other correlations have been noted for inorganic compounds.[5,6] Since e^2qQ depends on the imbalance in 5p orbital population and δ is dependent on both 5s and 5p population, due to shielding, it seems useful to combine these two parameters to clarify the chemical information inherent in the data. While attempts along these lines were made for $SbCl_5$ adducts,[6] the conclusions remained qualitative. Our approach in the present work is most closely related to that of Williams and Kocher[7] for tetrahedral Sn(IV). However, their efforts to combine ^{119}Sn Mössbauer data and halogen NQR results to obtain the valence orbital population at Sn were complicated by uncertainty as to the tetrahedral geometry in some of their compounds[8] and by their use originally of an incorrect value for $\Delta R/R$ for ^{119}Sn.[7,9] The idea of their calculations, to obtain electron populations at Sn in the valence orbitals directed toward the ligands, seems a useful one, easily understood chemically, and of interest in interpreting bonding, even though the numerical values may differ from those estimated in other ways.

In the present paper we restrict our experimental work to compounds containing Cl–Sb and R–Sb bonds, R being phenyl or substituted phenyl, but of two geometries, trigonal bipyramidal and octahedral. These data have been analyzed by a new, general method for obtaining orbital populations. We have also applied the analysis to several widely differing series of antimony compounds previously reported in the literature.

Experimental Section

With the exception of triphenylantimony dichloride (Eastman Organic Chemicals), the compounds for which Mössbauer spectra are reported were all prepared by known methods.[10,11] The trichlorides (R_2SbCl_3) were obtained as the monohydrates and dehydrated in vacuo at 100 °C[10] to give a weight loss in agreement with theory. The purity of these monohydrates and of the other compounds used was checked by elemental analyses, which agreed closely with theoretical values in all cases.

Table I. Mössbauer Parameters at 4 K[a]

Compd	Intensity, %	Γ (±0.08), mm s^{-1}	δ (±0.05), mm s^{-1}	e^2qQ (±0.5), mm s^{-1}	χ^2 per point
$pyH^+(PhSbCl_5^-)$	36	2.63	4.23	12.3	0.96
$pyH^+(Ph_2SbCl_4^-)$	41	2.51	2.73	24.9	1.03
Ph_2SbCl_3[b]	28	3.10	1.95	25.3	1.47
(p-FC_6H_4)-$PhSbCl_3$	39	2.63	2.08	25.4	1.04[c]
(p-$CH_3C_6H_4$)-$PhSbCl_3$	36	3.07	1.85	26.8	1.08
Ph_3SbCl_2[d]	27	2.42	2.80	−20.5	1.01
Ph_4SbCl[e]	24	2.74	3.61	−6.6	0.97

[a] Isomer shifts, δ, relative to InSb. All samples were about 10 mg of Sb cm^{-2}. [b] Ph_2SbCl_3 has been reported previously by Ruddick et al.[1] as $\delta = 1.5$,[f] $e^2qQ = 25.9$, and by Gukasyan et al.[13] as $\delta = 2.3$, $e^2qQ = 24.8$. [c] This fit required an additional intensity parameter. Due probably to a thickness effect,[15] the ratio of $\Delta m = 0$ to $\Delta m = 1$ intensities is 1.30. This parameter reduced χ^2 appreciably but hardly affected the values of δ or e^2qQ. In none of the others was this needed, and in none of these compounds did a nonzero value of the asymmetry parameter, η, improve the fit. [d] Ph_3SbCl_2 has been reported previously by us[14] as $\delta = 2.5$,[f] $e^2qQ = 20.6$, and by Gukasyan et al.[13] as $\delta = 2.8$, $e^2qQ = -21.7$. [e] Ph_4SbCl has been reported previously by us[14] as $\delta = 3.2$,[f] $e^2qQ = -6.0$, and by Ruddick et al.[1] as $\delta = 3.3$,[f] $e^2qQ = -6.4$. [f] Using −8.5 mm s^{-1} as conversion to InSb[5].

Our liquid helium cryostat, spectral procedures, and data analysis have been described previously.[12] The only major modification has been the addition of an Austin Science Associates laser interferometer, LC-9, and multiplexer, MP-9, to intersperse velocity information every 16th channel of the 512-channel analyzer. We have revised our program to fit each half of the laser points to a cubic equation for velocity vs. channel, and from this to calculate the velocity for each counting channel. A cosine correction was made to account for the finite geometry (less than 2% change in velocity, very small effect on baseline due to the limited source strength). The new analysis procedure has been checked periodically with metallic iron foils and gives results in good agreement with literature values. A linear relation between velocity and channel proved to be inadequate, although the cubic term did not appreciably improve the fit. Typically the standard deviation for velocity in the laser data (for maximum velocity set at ~14 mm s^{-1}) was 0.1 mm s^{-1} for the linear fit, 0.04 mm s^{-1} for the quadratic, and 0.03 mm s^{-1} for the cubic. By repeated runs with the laser system we have obtained a more accurate value for the isomer shift of InSb with our $Ni_{21}Sn_2B_6$(^{121}Sb) source, −1.65 ± 0.02 mm s^{-1} (the previous value used was −1.68[12]). The new Mössbauer spectral data are given in Table I. Four of these are reported for the first time and three are compounds whose spectra have been reported previously.[1,13,14] It should be noted that all of these compounds have experimental shifts with our source of less than 3 mm s^{-1}. Since earlier data were recorded with oxide sources and much larger experimental

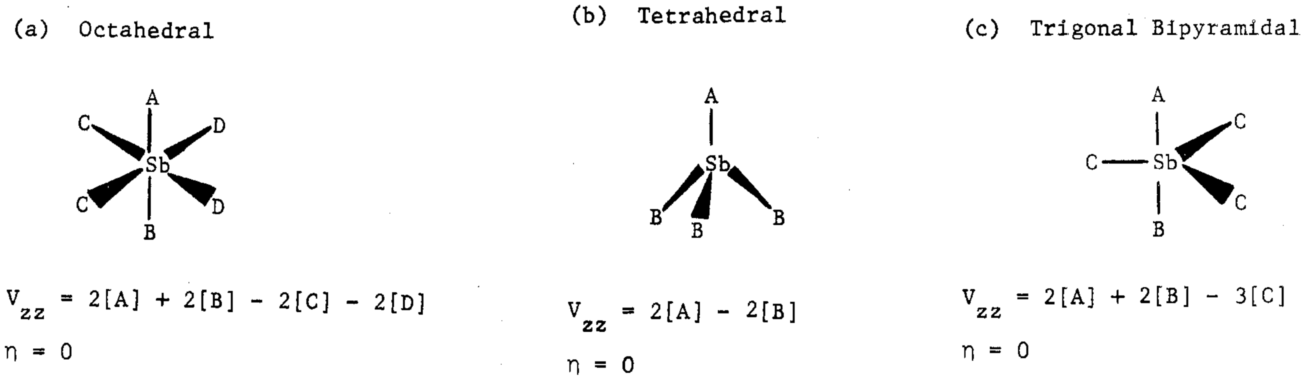

Figure 1. Additive field gradients for three geometries in terms of partial field gradient (PFG) parameters [L]. The z axis is vertical.

shifts, it was felt important to have a series of spectra obtained under similar conditions.

Orbital Population Analysis

Over a limited range the valence electron density at the Sb nucleus, $\psi^2(0)$, should be approximated by a linear function of the 5s population n_s, corrected for 5p shielding: $\psi^2(0) = n_s(a - bn_p)$. Around the configuration $5s^1p^2$, expected for organoantimony(V) compounds, the Hartree–Fock calculations of Ruby et al.[16] are best fit by the equation

$$\psi^2(0) = n_s(24.23 - 2.13n_p)a_0^{-3} \tag{1}$$

where a_0 is the Bohr radius. The isomer shift δ is given relative to $n_s = 0$ by[16]

$$\delta\ (\text{mm s}^{-1}) = [874a_0^3][\Delta R/R][\psi^2(0)] \tag{2}$$

The nuclear radius factor, $\Delta R/R$, has been estimated recently by several independent methods[5,17] as about -10^{-3}. We use in the present work the value -1.1×10^{-3}, based on a combination of Emery and Perlman's value for Sn[9] with Ruby and Shenoy's ratio for Sb to Sn.[18] Thus we have

$$\delta\ (\text{mm s}^{-1}) = -n_s(23.3 - 2.0n_p) \tag{3}$$

It is more appropriate to have δ relative to a measurable compound. If InSb is assumed to have the exact configuration $5s^1p^3$ (an assumption made by most previous workers with ^{121}Sb[5,16,17]), then

$$\delta(\text{relative to InSb}) = 17.3 - n_s(23.3 - 2.0n_p) \tag{4}$$

and

$$\delta(\text{relative to BaSnO}_3) = 8.8 - n_s(23.3 - 2.0n_p) \tag{5}$$

using the shift for InSb relative to $BaSnO_3$ (or $CaSnO_3$) as -8.5 mm s^{-1}.[5] Although this calibration depends strongly on both the choice of $\Delta R/R$ and the InSb configuration, the trends in n_s and n_p will be similar for a considerable range of these parameters. Equations 4 and 5 naturally will *not* apply to Sb(III) compounds, which have $n_s > 1$ and a larger p shielding effect.[16]

To relate n_s and n_p to orbital populations and to V_{zz} we use the localized molecular orbital approach of Clark et al.[3,19] The ground-state configuration is assumed to consist of localized orbitals directed along the Sb–ligand bonds. Each orbital ϕ_L is a linear combination of an Sb hybrid atomic orbital h_L and a ligand orbital χ_L: $\phi_L = c_1h_L + c_2\chi_L$. The Sb orbital population in h_L is $\sigma_L = 2c_1^2$ (σ_L is equivalent to Williams and Kocher's[7] α_L in the tetrahedral case), where h_L is an appropriate hybrid atomic orbital for the Sb geometry;[19] i.e.

$$h_L(\text{octahedral}) = \frac{1}{\sqrt{6}}s + \frac{1}{\sqrt{2}}p_z + \frac{1}{\sqrt{3}}d_{z^2} \tag{6a}$$

$$h_L(\text{tetrahedral}) = \frac{1}{2}s + \frac{\sqrt{3}}{2}p_z \tag{6b}$$

$$h_L(\text{tbp, apical}) = \frac{\cos\theta}{\sqrt{2}}s + \frac{1}{\sqrt{2}}p_z + \frac{\sin\theta}{\sqrt{2}}d_{z^2} \tag{6c}$$

$$h_L(\text{tbp, equatorial}) = \frac{\sin\theta}{\sqrt{3}}s + \frac{\sqrt{2}}{\sqrt{3}}p_z + \frac{\cos\theta}{2\sqrt{3}}d_{z^2} - \frac{\cos\theta}{2}d_{x^2-y^2} \tag{6d}$$

θ being the s–d mixing parameter for trigonal-bipyramidal geometry. From these orbitals the contribution of the Sb–L bond to n_s and n_p is

$$\text{octahedral:}\quad n_s = \sigma_L/6,\ n_p = \sigma_L/2 \tag{7a}$$

$$\text{tetrahedral:}\quad n_s = \sigma_L/4,\ n_p = 3\sigma_L/4 \tag{7b}$$

$$\text{tbp, apical:}\quad n_s = ((\cos^2\theta)/2)\sigma_L,\ n_p = \sigma_L/2 \tag{7c}$$

$$\text{tbp, equatorial:}\quad n_s = ((\sin^2\theta)/3)\sigma_L,\ n_p = 2\sigma_L/3 \tag{7d}$$

Before relating the measured e^2qQ to the orbital populations, σ_L, we summarize pertinent results of the additive model for field gradients. We take the principal component of the field gradient tensor, $V_{zz} \equiv eq$, as equal in magnitude but opposite in sign to e^2qQ.[1] Since the quadrupole moment, Q, is negative for ^{121}Sb, this gives V_{zz} its correct sign but multiplies by the scale factor $e|Q|c/E_\gamma$. For the additive model applied to Sb(V), V_{zz} is made up of contributions directed along the Sb–ligand bonds. These contributions have been tabulated for many geometrical combinations by Bancroft and Platt.[3] The cases of interest in the present work are shown in Figure 1. The PFG [L] is characteristic not only of a given ligand L but also of the geometry. From e^2qQ data on trigonal-bipyramidal Sb(V) molecules, Ruddick et al.[1] have tabulated [L] values for a number of ligands. We note that our new data on $PhSbCl_5^-$ and $Ph_2SbCl_2^-$ (Table I) allow calculation of [Ph] for octahedral geometry. Referred to [Cl] = 0, [Ph] = -6.2 mm s^{-1} for the latter, appreciably different from the -7.0 ± 0.2 mm s^{-1} reported for [Ph] in trigonal bipyramids.[1] Since V_{zz} is negative in both the octahedral salts and in almost exactly the ratio 1:2 for the mono- and diphenyl compounds and since $\eta = 0$, the geometry must be close to regular octahedral with the diphenyl salt trans,[4] the principal axis in both cases being along the Ph–Sb bonds (see Figure 1). This is just the opposite from Ph_3SbCl_2, which has V_{zz} positive and the

z axis along the Cl–Sb bonds.[1,14]

The PFG contributions [L] for the geometries in Figure 1 have been given in terms of σ_L by Clark et al.[19] Defining a scale factor $K = (e^2c/E_\gamma)|Q|\langle r^{-3}\rangle_p$, where $\langle r^{-3}\rangle_p$ is the effective average value over the 5p radius r, corrected for the Sternheimer effect,[19] we obtain (neglecting 5d orbital contributions)

$$\text{octahedral:}\quad [L] = -(1/5)K\sigma_L \tag{8a}$$

$$\text{tetrahedral:}\quad [L] = -(3/10)K\sigma_L \tag{8b}$$

$$\text{tbp, apical:}\quad [L]^{ap} = -(1/5)K\sigma_L \tag{8c}$$

$$\text{tbp, equatorial:}\quad [L]^{eq} = -(4/15)K\sigma_L \tag{8d}$$

For the configurations shown in Figure 1 therefore

$$\begin{aligned}\text{octahedral:}\quad & V_{zz} = -(2/5)K(\sigma_A + \sigma_B - \sigma_C - \sigma_D)\\ & n_s = (1/6)(\sigma_A + \sigma_B + 2\sigma_C + 2\sigma_D)\\ & n_p = 3n_s\end{aligned} \tag{9}$$

$$\begin{aligned}\text{tetrahedral:}\quad & V_{zz} = -(3/5)K(\sigma_A - \sigma_B)\\ & n_s = (1/4)(\sigma_A + 3\sigma_B),\ n_p = 3n_s\end{aligned} \tag{10}$$

$$\begin{aligned}\text{tbp:}\quad & V_{zz} = -(2/5)K(\sigma_A + \sigma_B - 2\sigma_C)\\ & n_s = ((\cos^2\theta)/2)(\sigma_A + \sigma_B) + (\sin^2\theta)\sigma_C\\ & n_p = (1/2)(\sigma_A + \sigma_B) + 2\sigma_C\end{aligned} \tag{11}$$

Clearly the two measured quantities $e^2qQ = -V_{zz}$ and δ are not adequate to determine all of the σ values for a given compound. Even in a group of related compounds, in general, only relative trends for the σ's will be clearly found. However, by considering the relationships found between Sb and Sn Mössbauer parameters[2,20] and halogen NQR results on some of the Sb compounds[21-25] we can obtain σ values which are consistent with a large body of experimental data.

Results of Population Analysis

The adjustable parameters of this analysis are $\Delta R/R$ for the isomer shift, K for e^2qQ, and $\cos^2\theta$ for the trigonal-bipyramidal molecules. A large body of experimental data and a variety of calculations[5,17] support our choice of $\Delta R/R$, but it has moderate uncertainty. In determining a value for K, we note the observation by Bancroft et al.[20] that a plot of e^2qQ for Sb(V) vs. e^2qQ for Sn(IV) isoelectronic compounds has a slope of 3.4 and essentially zero intercept. Since several geometries and ligand combinations fit this plot, this suggests that σ_L is about the same for Sb and Sn in a given geometry, and (eq 9–11) $K_{Sb} = 3.4K_{Sn}$. The parameter $\Delta_0 = (2/5)K$[19] and has been reported for Sn as 5.5[7] and 4.3[8] mm s^{-1}, which gives K_{Sb} = 47 and 37 mm s^{-1}, respectively. All the *major* trends in the variety of Sb compounds to be considered would be exhibited for either choice of K. The lower value of 37 mm s^{-1} enhances the difference between σ's for electronegative and organic groups for a given V_{zz}, and our present calculations are made using that value. The choice of $\cos^2\theta = 0.4$ for R_3SbX_2 compounds depends on K as described below. Halogen NQR data are available for a number of the pertinent compounds. For $SbCl_6^-$ anions the observed frequency for ^{35}Cl is 23.7 ± 0.7 MHz[22] which gives, assuming $\eta = 0$, $e^2qQ = 47.3 \pm 1.4$ MHz. In the usual Townes–Dailey approximation[7,26] $\sigma_{Cl} = e^2qQ/e^2q_0Q$ for ^{35}Cl, where $e^2qQ = 2\nu$ and e^2q_0Q is the atomic coupling constant.[26] This approximation assumes pure p character in the Cl valence orbitals and no π interaction with the Sb atomic orbitals and gives for $SbCl_6^-$ an Sb orbital population of 0.43. The Mössbauer results of Friedt et al.[6] give $\sigma_{Cl} = 0.58$ (see Table VI), using $\Delta R/R = -1.1 \times 10^{-3}$. This result is independent of K or $\cos^2\theta$ and depends only on $\Delta R/R$. To make the latter agree with NQR a value of $\Delta R/R = -0.76 \times 10^{-3}$ would be required. Since this seems too small to fit the observed range in isomer shifts,[5,17] we conclude that the difference is a real effect of the different approximations used. For example, anion–anion repulsion will partially quench the field gradient measured at Cl (NQR) but not that from Mössbauer data. If, however, the Sb–Cl bond can be considered additive in different compounds, the ratio should be about the same regardless of compound. The ratios of σ_{Cl} and σ_{Br} from Mössbauer data on octahedral $SbCl_5L$[6] and trigonal-bipyramidal R_3SbX_2[14,15] compounds to σ_{Cl} and σ_{Br} calculated from available NQR data[21-25] are given in Table II. The $SbCl_5L$ compounds are not very sensitive to the choice for K: $SbCl_5NCCH_3$, for example, gives $\sigma_{Cl} = 0.66$ for $K = 47$ mm s^{-1}, rather than 0.68. However, the distinctive increase in σ_{Cl} between $SbCl_6^-$ and the adduct compounds is mirrored by both NQR and Mössbauer results, within a wide range of K. Thus, for the R_3SbX_2 compounds on which NQR data are available, we pick the value of $\cos^2\theta$ which also gives about the same ratio, $\cos^2\theta = 0.4$ (Table II). Note that both NQR and Mössbauer values of σ_X for these are considerably *lower* than for $SbCl_6^-$. Slightly better agreement for these ratios could be achieved by varying $\cos^2\theta$, but within <0.1 the value 0.4 is best. This selection does depend on the choice of K; for $K = 47$ the best value to give agreement with NQR ratios is $\cos^2\theta \approx 0.3$.

Table II. Comparison of Mössbauer and NQR Halogen Orbital Populations

Compd	σ_X(NQR)[a]	σ_X (Mössbauer)[b]	σ ratio (Mössbauer: NQR)
$KSbCl_6$	0.43[c]	0.58	1.35
$SbCl_5NCCH_3$	0.48	0.68	1.42
$SbCl_5NCCl$	0.48	0.66	1.38
Ph_3SbCl_2	0.30	0.38	1.27
Ph_3SbBr_2	0.33	0.42	1.27
Me_3SbBr_2	0.30	0.40	1.33

[a] Halogen NQR data from ref 21-25. The σ_X refers to σ_{Cl} or σ_{Br} and is calculated assuming no π interaction with the halogen. [b] Calculated assuming $K = 37$ mm s^{-1} and for the trigonal bipyramids $\cos^2\theta = 0.04$. See Tables III–VI. [c] Average for several $SbCl_6^-$ salts, not including K$^+$ specifically.[22]

Table III. Orbital Populations in Chloroorganoantimony Compounds[a]

Compd	n_s	n_p	σ_{Ph}	σ_{Cl}	K'/K	Other
$KSbCl_6$[b]	0.58	1.74		0.58		
$pyH^+(PhSbCl_5^-)$	0.68	2.04	1.37	0.54		
$pyH^+(Ph_2SbCl_4^-)$	0.79	2.37	1.35	0.51		
Ph_2SbCl_3	0.84	2.52	(1.35)	(0.51)	0.73	$\sigma'_{Cl} = 0.66$
p-$FC_6H_4PhSbCl_3$	0.83	2.49	(1.35)	(0.51)	0.62	$\sigma_{p\text{-}FPh} = 1.29$[c]
p-$CH_3C_6H_4PhSbCl_3$	0.85	2.55	(1.35)	(0.51)	0.67	$\sigma_{p\text{-}CH_3Ph} = 1.41$[c]
Ph_3SbCl_2						
$\cos^2\theta = 0.00$	0.71	1.44	0.71	0.02		
0.40[d]	0.79	2.52	1.07	0.38		
0.50	0.82	2.82	1.17	0.48		
0.70	0.88	3.39	1.36	0.67		
Ph_4SbCl						
$\cos^2\theta = 0.00$	0.72	1.94	0.72	0.27		
0.40[d]	0.73	2.27	0.83	0.38		
0.60	0.74	2.41	0.88	0.43		
0.80	0.75	2.57	0.93	0.48		

[a] Calculated assuming $K = 37$ mm s^{-1}. [b] Data from ref 6. [c] Assuming $\sigma'_{Cl} = 0.66$ for the bridging Cl. [d] Preferred fit.

The octahedral pyridinium salts (Table I) can be analyzed without regard to the $\cos^2\theta$ parameter, using $K = 37$ mm s^{-1}. A value for $\sigma_{Ph} - \sigma_{Cl} \approx 0.84$ is calculated from V_{zz} for both mono- and diphenyl compounds (eq 9). Since $n_p = 3n_s$, the measured δ gives n_s (eq 4), and thus σ_{Ph} and σ_{Cl} can be calculated for each (Table III). In the series $SbCl_6^-$, $PhSbCl_5^-$, $Ph_2SbCl_4^-$ the σ_{Cl} decreases slightly while σ_{Ph} is about constant. This trend is less pronounced but agrees with that observed for $Ph_{4-m}SnCl_m$ by Williams and Kocher.[7] Their values for σ_{Ph} and σ_{Cl} are of comparable magnitude, although, due to different stoichiometry, not directly comparable.

The compound Ph_2SbCl_3 was reported by Sams et al.,[1] but its structure was not known at that time and they did no detailed analysis, only indicating the possibility of bridging Cl's. Gukasyan et al.[13] interpreted their Mössbauer results on the same compound in terms of a trigonal-bipyramidal structure with Cl's in the equatorial plane. Since the crystal structure has now been determined,[27] we can interpret the Mössbauer data with some assurance. The molecule is dimeric with a single type of Sb site. The coordination about Sb is octahedral, with only small (8° or less) deviations from regularity. The two bridging Cl's (D in Figure 1a) are essentially coplanar with the nonbridging (C). Each Sb–Ph bond (A and B) makes angles of 91 and 97° with the nonbridging Cl's. The bridging Cl–Sb bond distances (2.62, 2.84 Å) are appreciably longer than the nonbridging (2.35, 2.39 Å). Using from $Ph_2SbCl_4^-$ the value $[Ph]^{oct} = -6.2$ mm s^{-1} (see previous section), a PFG value of +0.2 is calculated for the bridging Cl. The distortions from regularity do not appreciably affect V_{zz} and have been ignored: the exact bond angles predict a factor $3.9[Ph]^{oct}$ rather than $4[Ph]^{oct}$ as in Figure 1. The similarity of e^2qQ and δ for the two substituted trichloro compounds to those of Ph_2SbCl_3 (Table I) indicates they also have an octahedral bridged structure. The positive PFG corresponds to the bridging Cl having slightly greater withdrawing effect on the Sb p electrons than a terminal Cl. However, the lower δ for the bridged compounds corresponds to increased 5s density, a seeming inconsistency.

Before proceeding further, we examine the comparison by Goel et al.[2] of $Me_3Sb(OCOR)_2$ with $Me_3Sn(OCOR)$ compounds, the latter known to contain bridging –OCOR groups. They found

$$(e^2qQ)_{Sb} = 4.48(e^2qQ)_{Sn} + 10.21 \qquad (12)$$

quite different from the relationship between isoelectronic Sb and Sn compounds[20] discussed earlier. However, the isomer shift values fall on the same line as the isoelectronic compounds, a fact which suggests that σ_X' for the bridging Sn–OCOR bond is about equal to σ_X for the nonbridging Sb–OCOR bond. In our model we suggest that the bridging group, being more distant from the central atom, may have a different effective K', since K is proportional to $\langle r^{-3}\rangle_p$. The e^2qQ relation (eq 12) can thus be expressed in terms of our model (eq 11) as

$$(4/5)K_{Sb}(\sigma_X - \sigma_{Me}) = 4.48(4/5)K_{Sn}\,[K'\sigma_X'/K_{Sn} - \sigma_{Me}'] + 10.21 \qquad (13)$$

This relation holds for a series of X groups, so that in addition to the bridging group $\sigma_X' = \sigma_X$ and σ_{Me}'(for Sn) = σ_{Me}(for Sb) for each, σ_{Me} must be about constant for the series. Previously we found $K_{Sb} = 3.4K_{Sn}$. Equating the first terms on both sides of eq 12 therefore gives $K'/K = 0.76$ for Sn–OCOR bridging groups. Equating the remaining terms gives $\sigma_{Me}K_{Sb} \simeq 40$ or $\sigma_{Me} \simeq 1.1$ for $K_{Sb} = 37$ mm s^{-1}. This latter value will be referred to again in discussion of trigonal-bipyramidal molecules. That K' should be lower than K follows if $\langle r^{-3}\rangle_p$ is smaller for bridging groups.

For Ph_2SbCl_3, the ratio of average bond distances[27] predicts $K'/K = (2.37/2.73)^3 = 0.65$ as a minimum value. By assuming σ_{Ph} and σ_{Cl} the same as in $Ph_2SbCl_4^-$, the data for Ph_2SbCl_3 can be used to give both σ_{Cl}' and K' for the bridging bonds using eq 9. In Table III are shown the results: $K'/K = 0.73$ and $\sigma_{Cl}' = 0.66$. The similarities of the K'/K ratio to that for Sn and to the bond distance ratio are gratifying. Since the bridging Cl has to donate to two Sb bonds, one might expect a smaller ligand character in each than in a nonbridging Sb–Cl bond, in agreement with the larger σ_{Cl}'. Taking σ_{Cl}' constant, the K'/K ratio and σ_R can be calculated for the substituted trichloro compounds (Table III). The variation in K'/K is more likely a reflection of uncertainty in the original data than a variation due to changing bond geometry. The average $K'/K = 0.67$, very close to the bond distance ratio for Ph_2SbCl_3. The σ_R values increase somewhat in the order $p\text{-}FC_6H_4 < C_6H_5 < p\text{-}CH_3C_6H_4$, indicating that $p\text{-}FC_6H_4$ gives the most ligand character to the Sb–C bond or is the least electron donating.

For the additive PFG model in trigonal-bipyramidal geometry $[Ph]^{ap} = (3/4)[Ph]^{eq}$ (see eq 8) and V_{zz} for Ph_4SbCl should be half that for Ph_3SbCl_2. This is not the case, and the experimental data require[1] $[Ph]^{ap} \approx [Ph]^{eq}$. It has been proposed that the more positive δ for Ph_4SbCl indicates more 5s character in its apical bonds than in Ph_3SbCl_2,[1] which would agree qualitatively with its small V_{zz}. The variation of hybridization can be expressed quantitatively by the mixing parameter θ (eq 6). A large $\cos^2\theta$ implies greater 5s character in the apical bonds and less in the equatorial. For Ph_3SbX_2, eqs 4 and 11 give

$$n_s = (17.3 - \delta)/(23.3 + 2v - 6v\cos^2\theta - 6n_s)$$
$$\sigma_{Ph} = n_s + v\cos^2\theta,\ \sigma_X = \sigma_{Ph} - v \qquad (14)$$

where $v = V_{zz}/0.8K$, while for Ph_4SbX, $v' = V_{zz}/0.4K$ and

$$n_s = (17.3 - \delta)/(23.3 + v' - 3v'\cos^2\theta - 6n_s)$$
$$\sigma^{eq}{}_{Ph} = n_s + v'\cos^2\theta/2,\ \sigma_X + \sigma^{ap}{}_{Ph} = 2\sigma^{eq}{}_{Ph} - v' \qquad (15)$$

For Ph_3SbCl_2 $v = 0.69$ and for Ph_4SbCl $v' = 0.45$, using $K = 37$ mm s^{-1}. Values of n_s and the σ's are shown in Table III for various selected $\cos^2\theta$. For Ph_3SbCl_2 a value of $\cos^2\theta$ between 0.5 and 0.7 would give closest agreement with σ_{Ph} and σ_{Cl} for the pyridinium salts. The Sn results,[7] however, lead one to expect a reduction in both σ's with the decreased number of Sb–Cl bonds. The choice of $\cos^2\theta$ is rather arbitrary unless one has further information. However, as noted earlier, the ratio between σ_{Cl} from Mössbauer data and that from ^{35}Cl NQR data for this compound[24] can be used to fix the value of $\cos^2\theta \approx 0.4$ (Table II). This, of course, means that about 40% of the Sb 5s orbital is utilized in the apical Sb–Cl bonds and 60% in the equatorial bonds to phenyl. Thus each of the five bonds has about equal 5s character. Also σ_{Ph} is lower than that for the pyridinium salts by about 20%, not by quite as much as σ_{Cl}. All values of $\cos^2\theta$ reduce $\sigma^{eq}{}_{Ph}$ even further in Ph_4SbCl. There is no fundamental reason why $\sigma^{eq}{}_{Ph}$ should equal $\sigma^{ap}{}_{Ph}$ in the latter compound (eq 15), but we have made this assumption in order to solve for σ_{Cl}. It is seen that the same $\cos^2\theta = 0.4$ gives a reasonable fit, with σ_{Cl} being about the same as for Ph_3SbCl_2 and the difference in Mössbauer parameters being caused by a change in the Sb orbital population of the phenyl bonds. As the number of phenyl bonds increases from 2 to 4, σ_{Ph} decreases; the approximate equality of σ_{Cl} in Ph_4SbCl and Ph_3SbCl_2 is mirrored by a similar equality for σ_{Ph} in $PhSbCl_5^-$ and $Ph_2SbCl_4^-$ (Table III). A variation in 5s character of the apical bonds (varying $\cos^2\theta$) does not seem necessary.

Choosing the simplest consistent set of parameters, we pick $\cos^2\theta \approx 0.40$ for both Ph_3SbX_2 and Ph_4SbX and extend the calculations to the other halogens (Table IV). These early data reported by us[14] had a constant isomer shift error which

Table IV. Orbital Populations in the Series Ph_3SbX_2 and Ph_4SbX[a]

Compd	δ[b]	e^2qQ[b]	n_s	n_p	σ_{Ph}	σ_X
Ph_3SbI_2	2.10	−18.1	0.84	2.63	1.08	0.47
Ph_3SbBr_2	2.50	−19.8	0.82	2.60	1.09	0.42
Ph_3SbCl_2[c]	(2.80)[b]	−20.6	0.79	2.51	1.07	0.37
Ph_3SbF_2	4.13	−22.0	0.70	2.26	1.00	0.26
Ph_4SbBr	3.30	−6.8	0.75	2.29	0.84	0.38
Ph_4SbCl[c]	3.56	−6.0	0.73	2.22	0.81	0.40
Ph_4SbF	4.26	−7.2	0.68	2.10	0.78	0.29

[a] Calculated assuming $K = 37$ mm s^{-1} and $\cos^2\theta = 0.40$. [b] Data from ref 14. Isomer shifts converted to InSb by using the value $\delta = 2.80$ mm s^{-1} for Ph_3SbCl_2 (Table I). [c] See also results based on present data (Table III).

Table V. Orbital Populations in Me_3SbX_2 Compounds[a]

Compd	δ[b]	e^2qQ	$\cos^2\theta$	n_s	n_p	σ_{Me}	σ_X
Me_3SbBr_2[c]	−6.17	−21.4	0.40	0.83	2.64	1.12	0.40
$Me_3Sb(OCOCF_3)_2$[d]	−5.5	−28.0	0.35[e]	0.76	2.35	1.10	0.15
			0.40	0.78	2.53	1.16	0.21
$Me_3Sb(OCOCH_3)_2$[d]	−5.17	−23.3	0.35	0.75	2.27	1.02	0.23
			0.40[e]	0.76	2.45	1.08	0.29

[a] Calculated assuming $K = 37$ mm s^{-1}. [b] The δ values are relative to $BaSnO_3$. [c] Reference 15. [d] Reference 2. [e] Preferred fit.

has been corrected by referring all δ's to the present value (Table I) for Ph_3SbCl_2. The results are consistent with those for the chloride compounds. A value of $\cos^2\theta = 0.40$ gives σ_{Ph} values which are about equal in each series but somewhat less in the tetraphenyl one. The values for σ_X vary about as expected with halogen electronegativity. Both σ_{Ph} and σ_F seem slightly low for Ph_3SbF_2 and perhaps indicate that compound has a slightly larger value for $\cos^2\theta$. This one borderline case is the only evidence for changes in hybridization in these series. In Ph_3SbBr_2 the value for σ_{Br} bears the same relation to that from the ^{81}Br NQR frequency[21] as the σ_{Cl} does to that from ^{35}Cl NQR for Ph_3SbCl_2 (Table II).

Related to the Ph_3SbX_2 series is the Me_3SbX_2 one reported by Goel et al.[2] where X = OCOR. These are also trigonal bipyramids with the X groups in apical positions. Unlike the phenyl series, δ varies only slightly with changing X and δ vs. e^2qQ has a small positive slope as compared to the much larger negative one in the former. This trend has been explained by assuming the Sb–O apical bonds have little 5s character; thus changing X primarily affects the 5p orbitals of Sb.[2] In Table V we have made calculations for the most extreme cases, X = $OCOCF_3$ and $OCOCH_3$. We also include Me_3SbBr_2 from data reported by Shenoy and Friedt.[15] For $\cos^2\theta = 0.40$ the latter gives $\sigma_{Br} = 0.40$ in appropriate ratio to ^{81}Br NQR data[25] (Table II) and also gives $\sigma_{Me} = 1.12$ in agreement with our earlier value 1.1 from e^2qQ for Sb vs. Sn. In the $Me_3Sb(OCOR)_2$ series as we have shown earlier, it seems likely that σ_{Me} is about constant. This would require a slight increase in $\cos^2\theta$ from X = $OCOCF_3$ to $OCOCH_3$. Choosing $\cos^2\theta = 0.35$ for the former and 0.40 for the latter, $\sigma_{Me} \approx 1.1$ for each, σ_X increases as expected, and n_s remains constant. According to this explanation changing X does primarily affect the 5p orbitals,[2] but the 5s character of the Sb–O bonds is *not* negligible and in fact is about the same as the apical bonds of the other R_3SbX_2 compounds. The value of n_s, and consequently δ, remains about constant due to slightly changing hybridization.

A quite different series also has a positive slope for δ vs. e^2qQ, the $SbCl_5$ adduct series reported by Friedt et al.[6] Although not all their complexes gave $\eta = 0$ experimentally, presumably those with $\eta = 0$ have geometry approaching octahedral, with the adduct ligand L along the *z* axis. Since L is a weak donor, one expects σ_L to be quite small, which indeed it is (Table VI). Friedt et al.[6] have proposed two alternate explanations for the trend observed. First they noted that a decrease in magnitude of e^2qQ and an increase in δ are both associated with increased donor ability of L. If the donation from L is primarily to a 5p orbital of Sb, this would decrease both V_{zz} and (due to shielding) the 5s density. Alternatively, they proposed that increased donation from L could cause an increase in the Sb–Cl bond ionicity which would affect e^2qQ and δ in the same way. In our model the octahedral geometry, unlike trigonal bipyramidal, has a fixed 5s character to the bonds, and thus the first explanation cannot be accommodated. Changes in Sb–Cl bond ionicity are equivalent to changes in σ_{Cl}. Thus the weak donor $NCCCl_3$ (Table VI) has the largest σ_{Cl}, or most covalent Sb–Cl bonds, while the somewhat stronger donor $OSMe_2$ has lower σ_{Cl}, and L = Cl^- in the $SbCl_6^-$ ion has the most ionic bonds. The agreement in trends with ^{35}Cl NQR data (Table II) has been mentioned earlier as reinforcing this interpretation.

Table VI. Orbital Populations in $SbCl_5L$ Compounds[a]

Compd	δ[b]	e^2qQ[b]	n_s	n_p	σ_{Cl}	σ_L
$SbCl_5NCCCl_3$	−3.01	−8.3	0.60	1.80	0.69	0.13
$SbCl_5NCCH_3$	−2.87	−7.9	0.59	1.77	0.68	0.15
$SbCl_5NCCl$	−2.66	−6.9	0.58	1.74	0.66	0.19
$SbCl_5OSMe_2$	−2.56	−5.3	0.57	1.71	0.63	0.27
$KSbCl_6$	−2.74		0.58	1.74	0.58	0.58

[a] Calculated assuming $K = 37$ mm s^{-1}. [b] Data from ref 6. The δ values are relative to $CaSnO_3$. These compounds all have $\eta = 0$ and are thus considered to be essentially octahedral.

The orbital population analysis method seems to be generally useful in a wide variety of Sb(V) compounds. We have given relations which apply to the most common geometries for Sb(V) and which also should be applicable with appropriate scaling to Sn(IV). Clearly our value of *K* and the relation between δ and n_s, n_p are tentative and should be improved to obtain "accurate" σ's. However, the general trends we have observed are unlikely to be affected: σ_{Ph} is approximately constant in a given type of compound but tends to increase as the number of electronegative groups attached to Sb increases, σ_{Me} is about equal to σ_{Ph} for a given type of compound, and the 5s character of the apical bonds in R_3SbX_2 and R_4SbX compounds is generally appreciable but varies only slightly among compounds. In the pentacoordinate compounds we have considered, the apical and equatorial bonds have about equal 5s character. In addition, bridging ligands have a smaller effective value of $\langle r^{-3}\rangle_p$ than nonbridging, K'/K being about 0.7. Clearly there are many effects, of which π bonding is only one, which we have not considered. However, most additional refinements would also add more parameters. The major advantage of the present analysis is that it enables a combination of both δ and e^2qQ to obtain parameters of chemical interest which can be compared among different geometries. From a practical standpoint, the more restrictive the conditions, the more manageable these comparisons. We have attempted to apply the method to enough cases so that its limitations as well as its usefulness may be seen.

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Registry No. $pyH^+(PhSbCl_5^-)$, 5425-93-4; $pyH^+(Ph_2SbCl_4^-)$, 58463-82-4; Ph_2SbCl_3, 54195-68-5; *p*-$FC_6H_4PhSbCl_3$, 58463-83-5; *p*-$CH_3C_6H_4PhSbCl_3$, 58463-84-6; Ph_3SbCl_2, 34716-91-1; Ph_4SbCl, 51153-49-2; ^{121}Sb, 14265-72-6.

References and Notes

(1) J. N. R. Ruddick, J. R. Sams, and J. C. Scott, *Inorg. Chem.*, **13**, 1503 (1974).
(2) R. G. Goel, J. N. R. Ruddick, and J. R. Sams, *J. Chem. Soc., Dalton Trans.*, 67 (1975).

(3) G. M. Bancroft and R. H. Platt, *Adv. Inorg. Chem. Radiochem.*, **15**, 59 (1972).
(4) J. N. R. Ruddick and J. R. Sams, *Inorg. Nucl. Chem. Lett.*, **11**, 229 (1975).
(5) L. H. Bowen in "Mössbauer Effect Data Index 1972", J. G. Stevens and V. E. Stevens, Ed., IFI/Plenum, New York, N.Y., 1973, p 71.
(6) J. M. Friedt, G. K. Shenoy, and M. Burgard, *J. Chem. Phys.*, **59**, 4468 (1973).
(7) D. E. Williams and C. W. Kocher, *J. Chem. Phys.*, **52**, 1480 (1970); **55**, 1491 (1971).
(8) A. G. Maddock and R. H. Platt, *J. Chem. Phys.*, **55**, 1490 (1971).
(9) G. T. Emery and M. L. Perlman, *Phys. Rev. B*, **1**, 3885 (1970).
(10) G. O. Doak and J. M. Summy, *J. Organomet. Chem.*, **55**, 143 (1973).
(11) G. O. Doak and H. G. Steinman, *J. Am. Chem. Soc.*, **68**, 1987 (1946); G. O. Doak, L. D. Freedman, and S. M. Efland, *ibid.*, **74**, 830 (1952); J. Chatt and F. G. A. Mann, *J. Chem. Soc.*, 1192 (1940).
(12) L. H. Bowen, K. A. Taylor, H. K. Chin, and G. G. Long, *J. Inorg. Nucl. Chem.*, **36**, 101 (1974).
(13) S. E. Gukasyan, V. P. Gorkov, P. N. Zaikin, and V. S. Shpinel, *J. Struct. Chem. (Engl. Transl.)*, **14**, 603 (1973).
(14) G. G. Long, J. G. Stevens, R. J. Tullbane, and L. H. Bowen, *J. Am. Chem. Soc.*, **92**, 4230 (1970).
(15) G. K. Shenoy and J. M. Friedt, *Phys. Rev. Lett.*, **31**, 419 (1973).
(16) S. L. Ruby, G. M. Kalvius, G. B. Beard, and R. E. Snyder, *Phys. Rev.*, **159**, 239 (1967).
(17) D. I. Baltrunas, S. P. Ionov, A. Y. Aleksandrov, and E. F. Makarov, *Chem. Phys. Lett.*, **20**, 55 (1973).
(18) S. L. Ruby and G. K. Shenoy, *Phys. Rev.*, **186**, 326 (1969).
(19) M. G. Clark, A. G. Maddock, and R. H. Platt, *J. Chem. Soc., Dalton Trans.*, 281 (1972).
(20) G. M. Bancroft, V. G. K. Das, and K. D. Butler, *J. Chem. Soc., Dalton Trans.*, 2355 (1974).
(21) T. B. Brill and G. G. Long, *Inorg. Chem.*, 9, 1980 (1970).
(22) R. F. Schneider and J. V. DiLorenzo, *J. Chem. Phys.*, **47**, 2343 (1967).
(23) M. Burgard and E. A. C. Lucken, *J. Mol. Struct.*, **14**, 397 (1972).
(24) D. L. Macalady, Ph.D. Thesis, University of Wisconsin, 1969, as quoted in ref 21.
(25) D. J. Parker, Ph.D. Thesis, University of Wisconsin, 1959, as quoted in ref 21.
(26) E. A. C. Lucken, "Nuclear Quadrupole Coupling Constants", Academic Press, New York, N.Y., 1969.
(27) J. Bordner, G. O. Doak, and J. R. Peters, Jr., *J. Am. Chem. Soc.*, **96**, 6763 (1974).

Contribution from the Research Department, Paulsboro Laboratory,
Mobil Research and Development Corporation, Paulsboro, New Jersey 08066, the Research Department,
Princeton Laboratory, Mobil Research and Development Corporation, Princeton, New Jersey 08540,
and the School of Chemical Sciences, University of Illinois, Urbana, Illinois 61801

Aluminum Removal from Dense Zeolites by Aqueous Chromium(III) Salt Solutions

W. E. GARWOOD, N. Y. CHEN, and JOHN C. BAILAR, Jr.*

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The porosity of a number of dense zeolites which occur as natural ores, such as erionite and phillipsite, as well as some made synthetically, such as zeolite T, is increased by dealuminization with hot aqueous solutions of chromium(III) salts. Crystallinity is not lost at aluminum removals up to about 40%. Porosity is increased still further when aluminum removal is followed by desilication with a solution of NaCl or NH_4Cl. The removal of aluminum can be understood if it is assumed that the hydrated chromium(III) ion penetrates into the pores of the zeolite where it complexes with the hydrolyzed aluminum and solubilizes it. Evidence for the formation of a complex is furnished by experiments on the dissolution of aluminum hydroxide powder by refluxing aqueous solutions of chromium(III) chloride.

Introduction

The crystal lattices of zeolites are known to be attacked by mineral acids with the formation of amorphous material.[1,2] Kerr has developed a special technique for dealuminization, using ethylenediaminetetraacetic acid (EDTA).[3]

In this paper, we describe a technique in which dealuminization is effected by solutions of chromium(III) salts. This was followed in selected cases by silica removal. Throughout the entire process, crystallinity was retained to a high degree.

Experimental Section

Procedure. Powdered zeolites were added to boiling solutions of chromium(III) salts (in most cases, chloride). At the end of the treatment period, the material was filtered through paper by suction and the filter cake was washed with water until the test for anion was negative. In all cases, the filtrate remained clear. The residue was dried overnight at 110 °C. Surface areas were measured by standard BET methods.

Materials. Hydrated chromium(III) chloride was obtained from Matheson Coleman and Bell. The green aqueous solutions turned blue-violet when they were allowed to stand or were heated, as was done before the addition of the zeolite. This change in color is due to an isomerization of the green salt (either $[Cr(H_2O)_5Cl]Cl_2{\cdot}H_2O$ or $[Cr(H_2O)_4Cl_2]Cl{\cdot}2H_2O$) to $[Cr(H_2O)_6]Cl_3$. The pH of a 1 N solution of the green salt was 1.9, while that of a corresponding solution of the violet-blue salt was 2.1.

The erionite came from Mt. Moses, Nev., and was shown by x-ray analysis to contain 20% clinoptilolite. Clinoptilolite, containing 20% phillipsite, was from the Mojave Desert. X-ray analyses showed that it also contained traces of silica and clay but no detectable phosphate.

Zeolite T was prepared by the procedure outlined in U.S. Patent 2950952 (Union Carbide). Its identity was shown by x-ray analysis.

The aluminum hydroxide powder was Baker's Analyzed Reagent grade.

Results

A. Erionite. 1. Removal of Aluminum by Chromium(III) Chloride. Aluminum removals between 8% and 64% were accomplished by contact of erionite with chromium(III) chloride solution (Table I). It is evident that removal of aluminum above 40% results in a considerable loss of crystallinity. It is also shown in Table I that clinoptilolite content is high in the dealuminized erionite, increasing from 20% in the original erionite to 30–40% after dealuminization.

2. Desilication Following Aluminum Removal. When the 38% dealuminized sample was refluxed with 1.0 N NaCl or 1.0 N NH_4Cl (150 ml of solution/g of zeolite), a portion of the silica in the structure was solubilized (Table II). The sorption capacity and the surface area increased in both steps.

3. Increase in Porosity. The nitrogen sorption isotherms (Figure 1) show the increase in porosity by successive removal of aluminum and silicon.

B. Clinoptilolite (Mixed with Phillipsite). The behavior of clinoptilolite (mixed with phillipsite) was similar to that of erionite (mixed with clinoptilolite) in that clinoptilolite content increased with dealuminization. Phillipsite was preferentially

* To whom correspondence should be addressed at the University of Illinois.