Contribution from the Department of Chemistry,
Wayne State University, Detroit, Michigan 48202

Hydrogen-1 Nuclear Magnetic Resonance and Mass Spectral Studies on Tricyclopropylaluminum Dimer and Mixed Methyl–Cyclopropylaluminum Compounds[1,2]

DAVID A. SANDERS, PAUL A. SCHERR, and JOHN P. OLIVER*

Received August 29, 1975 AIC50642P

Mass spectral, NMR, and infrared studies on tricyclopropylaluminum support a dimeric structure for the compound both in solution and in the gas phase. NMR studies on mixtures of trimethyl- and tricyclopropylaluminum demonstrate that the cyclopropyl group preferentially occupies the bridging position. Pentamethyl(cyclopropyl)aluminum dimer and tetramethyldi(cyclopropyl)aluminum have been identified by low-temperature NMR studies. Structural models are proposed for the mixed methyl–cyclopropylaluminum compounds on the basis of their NMR spectra and the known structure of tricyclopropylaluminum dimer. Bridge–terminal methyl group exchange in pentamethyl(cyclopropyl)aluminum is postulated to be an intramolecular process in toluene solution, proceeding with an Arrhenius activation energy of 15.8 ± 0.7 kcal/mol. A two-site averaging process of the terminal methyl groups in $Al_2(CH_3)_4(c\text{-}C_3H_5)_2$ was studied. It is proposed that this averaging process results from rotation of the bridging cyclopropyl groups. The Arrhenius activation energy for this process is approximately 11 kcal/mol. CNDO calculations for the proposed rotational process also lead to similar energy of activation and indicate that the most stable conformer in solution has the bridging cyclopropyl groups anti rather than syn as observed in the solid-state structure of tricyclopropylaluminum dimer.

Introduction

A topic of current interest in the study of electron-deficient bonded systems is the determination of the effect which various bridging groups have on the stability of the electron-deficient bridge system. It has been shown that unsaturated groups such as vinyl,[1–4] phenyl,[5,6] and phenylethnynyl,[5] all lead to enhanced stability of bridged aluminum and gallium compounds, while it has been shown that increasing the bulk of a saturated bridging group diminishes the stability of the bridge bond.[7]

It was suggested that the increased stability of unsaturated bridge systems results from the interaction of the nonbonding metal orbitals with the π orbitals of the bridging moiety[2] or by interactions resembling the Wheland intermediate in the case of phenylethynylaluminum.[5] These suggestions are in general accord with the reported structures of phenylaluminum derivatives,[8,9] but it is not clear that this is true for the phenylethynyl-bridged species in view of the recently reported structure.[10] Instead, it was suggested that the phenylethynyl group served as a π-electron donor to the bridge system, thus raising further questions about the types of interactions which may occur in these derivatives.

The most anomalous behavior of all, however, occurs in tricyclopropylaluminum, which although formally saturated with branching at the α-carbon atom, gives rise to bridged systems of unusual stability.[11] In this instance the structure has been shown to be compatible with interaction between the nonbonding metal orbitals of aluminum and the p orbitals of the α-carbon atom.[12]

In this paper additional information is presented on the ^1H NMR, ir, and mass spectra of tricyclopropylaluminum dimer and on mixed cyclopropylmethylaluminum systems. An unusual exchange process involving rotation of the bridging cyclopropyl groups is proposed as well as the intramolecular exchange of bridge and terminal methyl groups in pentamethylcyclopropyldialuminum.

Experimental Section

All manipulations were performed using standard vacuum-line techniques or in an argon or nitrogen filled drybox scavanged with Na–K alloy. All solvents were dried over sodium on the vacuum line before use.

Materials. Dicyclopropylmercury was prepared by the method of Reynolds et al.[13] Trimethylaluminum was obtained from Ethyl Corp., New York, N.Y., and used without further purification. Tricyclopropylaluminum was prepared by the reaction of excess aluminum metal dust with dicyclopropylmercury in a sealed Pyrex tube via the reaction shown in eq 1 in preference to the method previously described.[11]

$$2Al + 3Hg(c\text{-}C_3H_5)_2 \rightarrow Al_2(c\text{-}C_3H_5)_6 + 3Hg \qquad (1)$$

The reaction mixture was heated at 70 °C for 1 week. It was then worked up in the drybox by extracting the white crystalline material which had formed with hexane, filtering the solution through a coarse glass frit, and then transferring this solution to the vacuum systems where the solvent was removed leaving a white amorphous solid. This solid was purified by sublimation at 60 °C in a closed vessel evacuated to 10^{-5} Torr. The sublimation was allowed to proceed for 3–4 days, the sublimed clear crystals were removed, and the operation was repeated until no additional crystals sublimed from the reaction mixture. The crystals of tricyclopropylaluminum dimer were obtained in ~90% yield (mp 59–61 °C in a sealed capillary). The molecular weight determination, hydrolysis, and aluminum analysis were reported previously.[11]

NMR Spectra. NMR samples were prepared by addition of tricyclopropylaluminum to NMR tubes in the drybox which were then transferred to the vacuum system where solvent and volumetrically measured quantities of trimethylaluminum were added. A small amount of cyclopentane was used as an internal line width standard in most samples.

The NMR spectra were recorded on a Varian A-60A spectrometer equipped with a variable-temperature probe. Line positions were obtained by linear interpolation between audiofrequency side bands of the methyl peak of toluene. Chemical shifts are reported as δ (ppm) upfield from the toluene methyl resonance. This line is 2.318 ppm downfield from TMS. The data collected in the tables have been corrected to the TMS standard.

Temperatures were calibrated using the chemical shift separation obtained from a specially prepared sample of methanol (containing 0.03% (v/v) of HCl) by linear interpolation between audiofrequency side bands. The relationship developed by Van Geet[14] was used to correlate chemical shift separation with temperature. The relative concentrations of the two aluminum compounds in a given sample were determined by integration. The total concentration of alkylaluminum dimers in toluene ranged from 0.1 to 2.8 M and was not critically adjusted as long as the samples were not viscous at −75 °C. In the mixed methyl(cyclopropyl)aluminum compounds only the methyl region was calibrated as the cyclopropyl regions were broad and inconsistent in structure due to the several different species present. The chemical shifts of the terminal and bridging methyl groups are linearly dependent on the concentration. The chemical shifts displayed in Figures 1 and 3 have been corrected to their approximate values for a 2 M toluene solution by extrapolation of a plot of chemical shift vs. concentration of dimers.

Kinetic measurements and lifetimes were obtained by standard NMR line-broadening techniques.[15] In the region of slow exchange the approximation[15,16] $1/\tau = \pi(\nu_{1/2} - \nu_{1/2}{}^0)$ was used to calculate

Table I. Comparison of Ir Frequencies in the Al–C Region (800–300 cm^{-1}) for Al_2Me_6, $Al_2(c\text{-}C_3H_5)_6$, and $Al_2(C_6H_5)_6$

$Al_2(CH_3)_6$[28]	$Al_2(c\text{-}C_3H_5)_6$	$Al_2(C_6H_5)_6$[29]
776 s	786 s	680 w
696 s	627 s	446 vs
604 s	608 m, sh	420 m
563 s	557 w	332 vs
	515 m	

lifetimes, where $\nu_{1/2}$ is the width at half-height of the peak under exchange conditions and where $\nu_{1/2}^0$ is the width at half-height when no exchange exists. $\nu_{1/2}^0$ varied between 1.2 and 2.0 Hz at low temperatures (~ −75 °C) depending upon the system. At these same temperatures the half-width of the internal standard cyclopentane was ~0.5 Hz.

For the self-exchange of pentamethyl(cyclopropyl)aluminum the line widths were measured only on the bridging methyl resonance as the terminal methyl resonances were obscured by other averaging processes. The kinetic parameters obtained from the line-broadening technique for the two-site averaging process displayed by dimethylcyclopropylaluminum dimer were confirmed by complete line-shape analysis for the methyl resonance spectra by use of modifications of the McConnell equations to simulate theoretical spectra.[16]

Mass Spectra. The mass spectrum of tricyclopropylaluminum dimer was recorded on an AEI MS-902 double-focusing high-resolution mass spectrometer. The sample was manually mounted on the ceramic tip of the probe in a drybox. Precautions were taken to ensure that the probe was not exposed to air by sealing the probe in a plastic bag in the drybox and then transferring the probe to the mounting on the spectrometer, which also was flushed with dry nitrogen. No peaks due to oxides or alkoxides were observed in the mass spectra. Mass spectra were recorded at 10, 12, 13, 15, 30, and 70 eV between 60 and 95 °C source temperatures. The source heater and filament were kept off until just prior to a run in order to keep the temperature low.

Infrared Spectra. The infrared spectra were recorded on a Perkin-Elmer Model 612 grating spectrophotometer. The spectrum of tricyclopropylaluminum dimer was run as a thin film (solid) between KBr plates. A few large crystals of $Al_2(c\text{-}C_3H_5)_6$ were placed on a KBr plate in a drybox and melted with the heat from a light bulb. The second KBr plate was then placed on the liquid and pressure was applied using the cell mounting. The common edge between the KBr plates was sealed with Cenco Plicene cement, mp 80 °C.

Ultraviolet Spectra. A Cary Model 14 recording spectrophotometer was employed for the uv spectra in the 2000–4000-Å range. Samples were run in 10-mm quartz cells using cyclohexane solvent.

Results and Discussion

Infrared Spectra. The infrared spectrum obtained on the solid tricyclopropylaluminum dimer showed absorptions at 515 (m), 557 (w), 608 (m, sh), 627 (s), 786 (s), 811 (s), 845–895 (s, br), 1016 (s), 1038 (s), 1188 (s), 1247 (s), 1434 (s), 1456 (m), 2867 (s), 2930 (s), 2975 (s), 3004 (s, sh), 3048 (s) cm^{-1} (s = strong, m = medium, w = weak, sh = shoulder, br = broad). These bands are similar to those recently reported by Müller et al.[17] and are in accord with the known structure[11] of the dimeric molecule and the absorptions characteristic of the cyclopropyl group which occur at 820, 860, 1025, 1480, and 3080 cm^{-1}.[18] A comparison of the frequencies in the Al–C region (800–300 cm^{-1}) of tricyclopropylaluminum with trimethyl- and triphenylaluminum is made in Table I.

Ultraviolet Spectra. Insufficient information is available to predict whether any uv absorption bands should be observed as a result of the interaction of the cyclopropyl group with the aluminum atoms. In the only somewhat analogous case, Cowley and Furtsch[19] predicted a band for the cyclopropyl group interacting with the vacant 2p orbital of boron but failed to observe any transition. Similarly, no uv absorption was observed in the 200–400-nm range for the tricyclopropylaluminum dimer.

Mass Spectra. The principal ions observed in the mass spectra of the tricyclopropylaluminum dimer obtained with 70- and 15-eV ionizing potentials are given in Table II. No parent dimer ion was detected even at low source temperature and low ionizing potential. The dimeric species $[Al_2(c\text{-}C_3H_5)_5]^+$ was present in high abundance at 70 eV and became the most prominent species observed in the 15-eV spectrum.

Table II. Relative Abundances of the Principal Positive Ions Formed in the Mass Spectrum of Tricyclopropylaluminum Dimer at 70 and 15 eV with a Source Temperature of 80–90 °C

m/e		Rel abund	
		70 eV	15 eV
27	Al^+	100	3.9
28	AlH^+	1.4	0.2
29	AlH_2^+	1.4	
39	$C_3H_3^+$	25	
40	$C_3H_4^+$	11	0.4
41	$c\text{-}C_3H_5^+$	32	1.5
42	$c\text{-}C_3H_6^+$	34	16
43	$c\text{-}C_3H_7^+$	2.9	0.6
55	$Al(C_2H_4)^+$	2.2	0.1
67	$Al(C_3H_4)^+$	24	7.1
68	$Al(c\text{-}C_3H_5)^+$	4.5	0.8
69	$Al(C_3H_5)H^+$	3.7	0.8
81	$Al(C_4H_6)^+$	1.2	0.2
83	$Al(C_4H_8)^+$	1.7	1.3
95	$Al_2(c\text{-}C_3H_5)^+$	0.8	
109	$Al(c\text{-}C_3H_5)_2^+$	55	90
110	$Al(c\text{-}C_3H_5)_2H$	4.0	6.7
122	$Al_3(c\text{-}C_4H_5)^+$	0.4	1.4
135	$Al_2(c\text{-}C_3H_5)(C_3H_4)^+$	0.7	0.1
149	$Al(c\text{-}C_3H_5)_2(C_3H_4)^+$	7.3	9.3
150	$Al(c\text{-}C_3H_5)_3^+$	2.9	1.1
177	$Al_2(c\text{-}C_3H_5)_3^+$	0.6	0.1
191	$Al(c\text{-}C_3H_5)_4^+$	1.5	0.3
217	$Al_2(c\text{-}C_3H_5)_3(C_3H_4)^+$	0.4	0.1
233	$Al(c\text{-}C_3H_5)_5H^+$	0.7	1.8
259	$Al_2(c\text{-}C_3H_5)_5^+$	41	100
260	$Al_2(c\text{-}C_3H_5)_5H^+$	7.3	21
275	$Al_3(c\text{-}C_3H_5)_4(C_2H_6)^+$	0.3	1.0

Table III. Metastable Reactions Observed in the Mass Spectrum of $Al_2(c\text{-}C_3H_5)_6$

	m/e	
Process	Obsd	Calcd
(weak) $Al_2(c\text{-}C_3H_5)_5^+ \rightarrow Al_2(c\text{-}C_3H_5)_3(C_3H_4)^+ + c\text{-}C_3H_6$	181.8	181.8
$Al_2(c\text{-}C_3H_5)_5^+ \rightarrow Al(c\text{-}C_3H_5)_4^+ + Al(c\text{-}C_3H_5)$	140.9	140.9
$Al(c\text{-}C_3H_5)_4^+ \rightarrow Al(c\text{-}C_3H_5)_2(C_3H_4)^+ + c\text{-}C_3H_6$	116.2	116.2
(weak) $Al_2(c\text{-}C_3H_5)_5^+ \rightarrow Al(c\text{-}C_3H_5)_2(C_3H_4)^+ + HAl(c\text{-}C_3H_5)_2$	85.7	85.7
(weak) $Al(c\text{-}C_3H_5)_3{\cdot}^+ \rightarrow Al(c\text{-}C_3H_5)_2^+ + c\text{-}C_3H_5{\cdot}$	79.2	79.2
(weak) $Al(c\text{-}C_3H_5)_2(C_3H_4)^+ \rightarrow Al(C_3H_4)_2^+ + c\text{-}C_3H_6$	76.8	76.8
$Al(c\text{-}C_3H_5)_2^+ \rightarrow Al(C_3H_4)^+ + c\text{-}C_3H_6$	41.2	41.2

The major fragmentation pattern for the tricyclopropylaluminum dimer results from the successive loss of cyclopropyl groups; however, a few metastable peaks were observed which resulted from more complex rearrangement processes. The metastable peaks which resulted from the ion decompositions are listed in Table III. These species are consistent with the species listed in Table II.

The observed high abundance of the dimeric ion $[Al_2(c\text{-}C_3H_5)_5]^+$ and the other dialuminum species such as $[Al_2(c\text{-}C_3H_5)_4]^+$ and $[Al_2(c\text{-}C_3H_5)_3]^+$ should be compared with the corresponding results obtained from the mass spectra of trimethyl-[20–22] and triphenylaluminum[23] and of hydride- or halide-bridged[24] species. In all of these cases the abundance of the dimeric fragments is substantially less, increasing from barely detectable level for the methyl species to significant but low abundances for the more strongly bridged hydrides and halides.

This contrast between the cyclopropyl-bridged species and the other aluminum derivatives is a strong indication of the ability of the cyclopropyl group to stabilize the dimeric de-

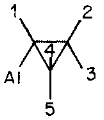
Table IV. Observed and Calculated NMR Parameters for Tricyclopropylaluminum Dimer

	Obsd chem shifts,[a,b,d] ppm				
Location	δ_1	δ_2	δ_3	Δ_{1-3}	Δ_{2-3}
Bridge	−1.567	1.080	1.481	−3.048	−0.401
Terminal	−1.310	0.536	0.241	−1.551	0.295

	Obsd coupling constants,[a,c,d] Hz					
Location	J_{12}	J_{13}	J_{23}	J_{24}	J_{25}	J_{35}
Bridge	9.31	7.49	−2.63	8.50	5.81	8.33
Terminal	10.34	7.70	−2.96	8.04	4.88	7.63

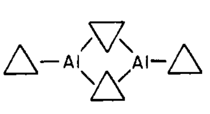
E_{neg}[f] of Al	Calcd coupling constants,[e] Hz					
	J_{12}	J_{13}	J_{23}	J_{24}	J_{25}	J_{35}
1.50	10.31	7.71	−2.85	8.12	4.32	7.34
1.70	9.92	7.24	−3.16	8.34	4.60	7.72
1.30	10.70	8.18	−2.53	7.90	4.03	6.95

[a] 12 mol % in toluene at 20 °C. [b] Chemical shifts were measured relative to the toluene methyl group and have been corrected to TMS as the standard by addition of 2.318 ppm. [c] Calculated using LACOON3. [d] The protons are assigned according to the diagram

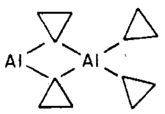


[e] Calculated from the expression $J_{xy} = aE_{\text{neg}} + b$; see ref 17. [f] The best value of the electronegativity of aluminum (1.50) was taken from F. Hruska, G. Kotowycz, and T. Schaefer, *Can. J. Chem.*, 43, 2827 (1965). The other values were chosen to show the effect of changes in electronegativity on the coupling constants.

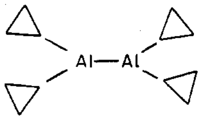
rivative. This fact and the observation of ions such as $[Al_2(c\text{-}C_3H_5)_4]^+$, which are represented by one of the structures I, II, or III, lead to the interesting possibility that



I



II



III

the cyclopropyl or similar stabilizing groups may permit the direct observation and possible isolation of subvalent aluminum compounds, I, such as those recently proposed by Eisch[25] in the photolysis of triphenylaluminum or the unknown but suggested metal–metal bonded species, III.[26]

It should be noted also that a low abundance of high-mass fragments, which appear to contain three aluminum atoms, was observed. This either may result from thermal decomposition yielding hydride species known to have trimeric or higher structures or may result from gas-phase intermolecular reactions.[24] Neither the source nor the structure of these can be confirmed from the present data.

NMR Studies. Initial reports already have appeared on the NMR spectra of tricyclopropylaluminum[11,27] and on the mixed methylcyclopropylaluminum system.[12] Here we wish to discuss these further and particularly the variety of exchange processes which are observed in these systems.

The NMR parameters for both the bridge and terminal groups for the tricyclopropylaluminum dimer are collected in Table IV along with the coupling constants calculated from the relationship $J_{HH} = aE_{\text{neg}} + b$.[27] A comparison of these values suggests major deviations from normal behavior for the bridging cyclopropyl group which cannot be accounted for by alteration of the electronegativity effect of the bridging site, as indicated by comparison of the observed coupling constants with those calculated for various electronegativities, but must arise from perturbation of the cyclopropyl group. This is further suggested by the substantial differences in chemical shifts, not only of the α proton but also of the two types of β protons on the bridging rings.

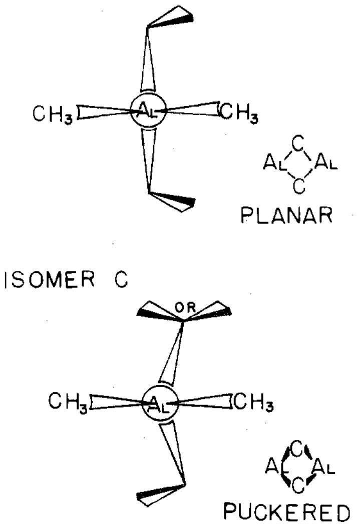


Figure 1. Proposed structures of mono- and dicyclopropylaluminum bridged dimers.

The changes in coupling constants can arise from the two related factors, the alteration in geometry about the ring and the change in the orbitals used in formation of the C–H bonds. Several factors may also contribute to the unusual chemical shifts. These include inductive effects which, on examination of a variety of monosubstituted cyclopropanes, suggests that protons 1, 3, and 5 should all be shifted slightly in the opposite direction. Possibly a better measure of this is to examine the internal chemical shifts. Again it has been shown that for a wide range of cyclopropyl derivatives Δ_{1-3} is large and negative for electropositive centers and positive for electronegative substituents, while Δ_{2-3} is positive and of the order of $^1/_2$ ppm for electropositive groups and negative with values up to ~0.4 ppm for very electronegative groups. Examination of the internal chemical shifts of the terminal group show them to be "normal" in behavior while the same internal shifts for the bridging group show divergent behavior.[27] Therefore, simple electronic effects cannot account for the chemical shifts of the bridging group.

The other factors which may play significant roles in the determination of the chemical shift are the anisotropy associated with the cyclopropyl group[28] and the relative orientation of the cyclopropyl groups with one another which determine their contribution to the chemical shift. Examination of Figure 1 shows that in the conformation adopted in the solid state proton 1 is relatively far from any of the cyclopropyl groups and probably should not be greatly affected and, if affected at all, should be shifted downfield. In the anti conformation proton 1 lies directly over the shielding region of the opposite ring at about 4 Å. Both the 2–4 and 3–5 sets of protons should be shifted downfield by the deshielding of the ring in either conformation. Clearly the observed changes may be accounted for qualitatively in these terms. The changes cannot be dealt with quantitatively since neither the exact structures nor the relative populations of the various conformers are known in solution, but certainly it would appear that both exist in solution and are undergoing rapid exchange as discussed below for the tetramethyldicyclopropyldialuminum and one may conclude further from the alteration in the coupling constants that significant changes have occurred in the hybrid orbitals used for bond formation in the bridging cyclopropyl group.

Mixed Methyl–Cyclopropylaluminum Systems. Mixing of trimethylaluminum with tricyclopropylaluminum leads to formation of a variety of species through intermolecular exchange as indicated in eq 2 with the value of *n* and the

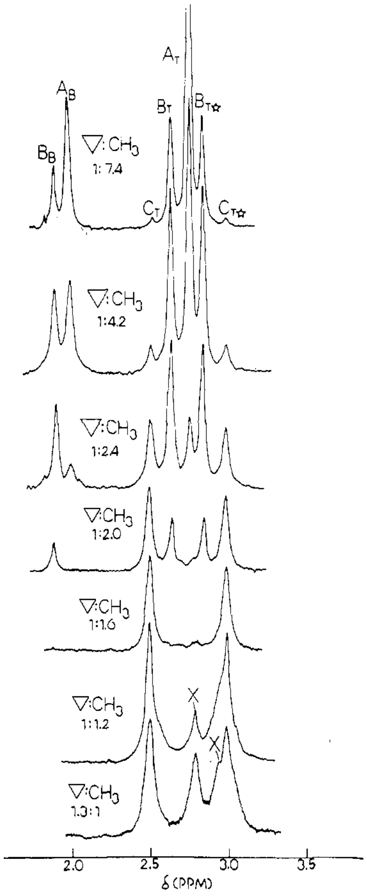


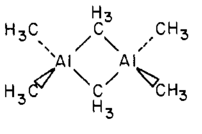
Figure 2. The 60-MHz NMR spectra of the methyl region of mixtures of trimethyl- and tricyclopropylaluminum dimers taken at −74 °C in toluene. The spectra show the various resonances associated with bridge and terminal sites on the nonexchanging dimers. The chemical shifts are given relative to the methyl group on toluene.

$$Al_2(CH_3)_6 + Al_2(c\text{-}C_3H_5)_6 \rightleftharpoons Al_2(CH_3)_n(c\text{-}C_3H_5)_{6-n} \quad (n = 1\text{-}5) \quad (2)$$

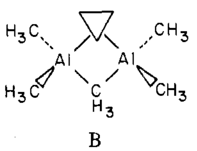
equilibrium constant dependent upon the solvent, temperature, and concentrations, as expected, as well as on the increased stability of the system with cyclopropyl groups located in the bridging positions.

In order to identify some of the species present in solution the low-temperature (−75 °C) NMR spectra of the methyl region of various mixtures of $Al_2(c\text{-}C_3H_5)_6$ and $Al_2(CH_3)_3$ are shown in Figure 2. The spectra display unusual features which indicate the variety of species present in solution. For example, as the cyclopropyl:methyl ratio is increased, certain peaks gain or lose intensity to the same extent. These peaks are assigned to the methyl protons of a particular species.

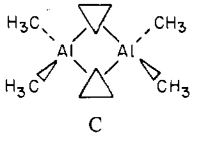
The peaks labeled A_T and A_B are always 2:1 to each other; B_T and B_{T^*} are always 1:1 to each other. These observations, plus consideration of the chemical shift separations, led us to the assignments of the peaks in Figure 2 and to structures A–D.



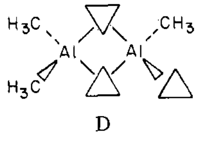
A



B



C



D

Subscripts T and B represent the terminal and bridging positions, respectively. Subscripts T and T* denote terminal methyl groups attached to the same aluminum atom but having different chemical shifts.

One can observe from Figure 2 the decreasing intensities of the bridging methyl peaks for A and B (δ 2.03 and 1.94, respectively) as the $c\text{-}C_3H_5$:CH_3 ratio is increased. At the ratio of 1:1.6 bridging methyl groups are no longer observable and we are left with only compound C, plus small amounts of D. If the distribution of cyclopropyl and methyl groups among the six positions were random, we would still observe a considerable fraction of bridging methyl groups in the 1:1.6 mixture. We can conclude, therefore, that the cyclopropyl groups prefer the bridging position over methyl groups. We do not observe any compounds with terminal cyclopropyl groups until both bridging positions are occupied by cyclopropyl groups.

The assignment of two different resonance frequencies to the terminal methyl groups in compounds B and C may be accounted for by consideration of the possible structures illustrated in Figure 1. These projections perpendicular to the Al–Al axis clearly show that the terminal methyl groups in compound B will be in different magnetic environments. This will also be true for compound C, provided that the cyclopropyl groups are oriented as they are in the solid state,[12] with both oriented on the same side of the Al–C–Al–C ring or with the ring retaining some type of puckered configuration.

At −75 °C, the spectra of samples with $c\text{-}C_3H_3$:CH_3 ratios greater than 1:1.6 show the emergence of two terminal cyclopropyl groups. The assignment of these lines to a particular compound is impossible with the existing data, as a large number of different isomers may exist on the basis of the structural models previously discussed. As the $c\text{-}C_3H_5$:CH_3 ratio is increased from 3:1 to 13:1, the lines due to C eventually disappear, leaving only the two extremely broadened peaks labeled X which are associated with various terminal methyl groups in compounds containing several cyclopropyl groups.

Clearly the variety of species present in this system provides an opportunity to examine a number of exchange reactions. We have already shown that the bridge–terminal exchange in tricyclopropylaluminum dimer is very slow relative to other alkyl-exchange reactions in aluminum systems on the NMR time scale and have implied that this shows a high value for the dissociation energy of dimer to monomer for this system, based on the assumption that this bridge–terminal exchange proceeds via the same type of dissociation mechanism proposed for trimethylaluminum.[1]

Turning our attention now to mixtures of (A) $Al_2(CH_3)_6$, (B) $(\mu\text{-}CH_3)(\mu\text{-}c\text{-}C_3H_5)Al_2(CH_3)_4$, and (C) $(\mu\text{-}c\text{-}C_3H_5)_2Al_2(CH_3)_4$ we can examine all other processes of interest to us. In Figure 3 we see the methyl resonances of a sample containing equilibrium mixtures of these three components as a function of temperature. At 80 °C all methyl resonances are coalesced, indicating rapid exchange of all groups. As the temperature is dropped, the resonance broadens and at 39 °C two lines are visible with the small upfield line occurring at the correct chemical shift (δ 2.82) for the averaged terminal methyl groups of C, the dicyclopropyl-bridged species. As the temperature is lowered further, the lines broaden, and at −6 °C a new broad line appears which is identified with B, $(\mu\text{-}CH_3)(\mu\text{-}c\text{-}C_3H_5)Al_2(CH_3)_4$, which splits into two resonances corresponding to the bridge and terminal methyl groups at −25 °C. The upfield terminal methyl groups overlap the terminal groups of C, but the resonance due to the bridging methyl group is clearly resolved and sharpens as the temperature is decreased with a chemical shift of δ 1.94.

Around −50 °C the self-exchange of trimethylaluminum is slowed sufficiently to give rise to two regions of resonance and

Table V. Kinetic Data for the Methyl Group Exchange in $Al_2(CH_3)_5(c\text{-}C_3H_5)$

Total dimer concn, M	$[Al_2(CH_3)_6]$, M	$[Al_2(CH_3)_5(c\text{-}C_3H_5)]$, M	$[Al_2(CH_3)_4(c\text{-}C_3H_5)_2]$, M	$[Al_2(CH_3)_5(c\text{-}C_3H_5)]/[Al_2(CH_3)_6]$	ΔE_a, kcal/mol	$1/\tau$,[a] s^{-1}	$\Delta S_a^{\ddagger}$,[a] eu	$\Delta H_a^{\ddagger}$,[a] kcal/mol
0.28	0	0.06	0.22	∞	16.2 ± 0.4	6.8	−9.2	15.7
0.90	Trace	0.36	0.54	30	16.5 ± 0.4	7.9	−10.2	16.0
0.45	0.07	0.24	0.14	3.4	14.4 ± 0.8	6.7	−1.8	13.9
1.9	0.30	1.02	0.58	3.4	15.2 ± 0.7	6.8	−5.2	14.7
2.2	1.0	0.99	0.21	1.0	16.7 ± 1.2	6.3	−11.1	16.2
0.30	0.14	0.14	0.02	1.0	16.2 ± 1.3	6.2	−9.0	15.7
0.38	0.20	0.10	0.08	0.5	15.0 ± 0.3	6.2	−4.2	14.5
2.8	1.72	0.93	0.15	0.5	15.9 ± 0.6	6.7	−10.0	15.4
					Av 15.8 ± 0.7	Av 6.7		

[a] Lifetimes, $\Delta S^{\ddagger}$, and $\Delta H^{\ddagger}$ values are given for −26 °C.

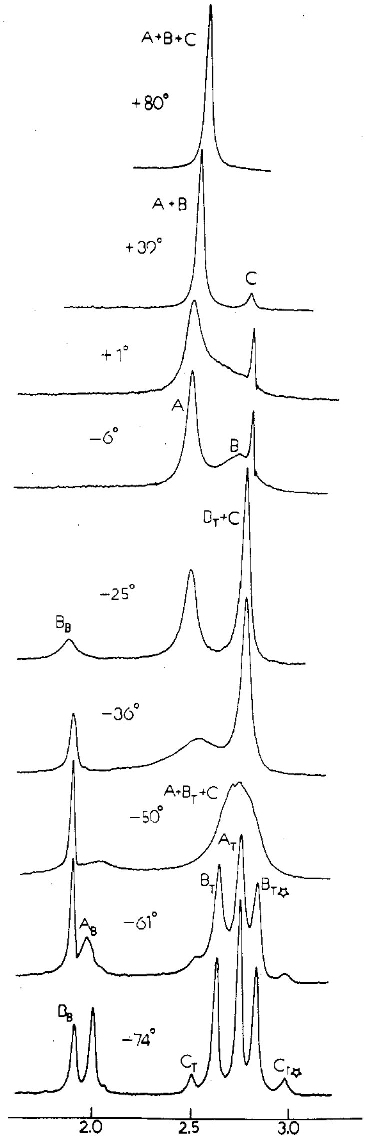


Figure 3. The 60-MHz NMR spectra of the methyl region of a sample containing ~5:1 trimethylaluminum–tricyclopropylaluminum as a function of temperature.

finally at −74 °C all exchange processes are sufficiently slow to permit observation of well-defined and identifiable lines for each type of methyl resonance.

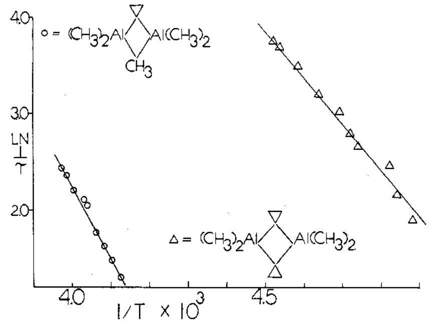


Figure 4. Arrhenius activation energy plots for the intramolecular bridge–terminal exchange in pentamethylcyclopropylaluminum and for the rotational averaging of the terminal groups in tetramethyldicyclopropylaluminum.

The changes are of major significance with regard to the various modes of exchange present since they show that the $Al_2(CH_3)_6$ present in solution does not exchange on the NMR time scale with $(\mu\text{-c-}C_3H_5)_2Al_2(CH_3)_4$ below 40 °C which clearly indicates that neither of the steps (eq 3 and 4) which

$$(\mu\text{-c-}C_3H_5)_2Al_2(CH_3)_4 \overset{\text{slow}}{\rightleftharpoons} 2(CH_3)_2(c\text{-}C_3H_5)Al \tag{3}$$

$$(CH_3)_3Al + (\mu\text{-c-}C_3H_5)_2Al_2(CH_3)_4 \not\rightarrow \tag{4}$$

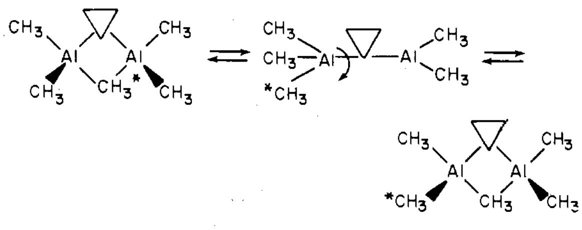
have been proposed as paths for alkyl exchange occur rapidly under these conditions. Further, at −25 °C the same statement can be made concerning the pentamethylcyclopropylaluminum which stops intermolecular exchange on the NMR time scale between −6 and −25 °C.

Finally some other averaging process occurs which does not involve intermolecular exchange both in tetramethyldicyclopropylaluminum and in pentamethylcyclopropylaluminum. This process results in distinguishing between the terminal sites in unsymmetrical species.

Let us now examine in a quantitative fashion the two unusual modes of exchange in this system. First we shall deal with the bridge–terminal exchange in $(\mu\text{-}CH_3)(\mu\text{-c-}C_3H_5)Al_2(CH_3)_4$ and compare this with the self-exchange in $Al_2(CH_3)_6$.

The results of exchange studies on pentamethylcyclopropylaluminum as a function of concentration are shown in Table V and an Arrhenius plot for the activation energy is given in Figure 4.

These results, coupled with the fact that intermolecular exchange with trimethylaluminum is slow under these conditions, lead to the proposed mechanism shown in eq 5. This mechanism is consistent with the negative entropy observed



(5)

Table VI. Kinetic Data for the Averaging Process in $Al_2Me_4(c\text{-}Pr)_2$

$[Al_2Me_4(c\text{-}Pr)_2]$, M	ΔE_a, kcal/mol	$1/\tau$,[a] s^{-1}	$\Delta S^{\ddagger}$,[a] eu	$\Delta H^{\ddagger}$,[a] kcal/mol
0.17	12.2 ± 0.5	15.4	−2.7	11.8
0.38	11.3 ± 0.7	13.9	1.7	10.9
0.90	9.4 ± 0.4	21.3	9.7	9.0

[a] Determined at −59 °C.

in this system which is similar to that observed both in the bridge–terminal exchange observed in μ-methyl-μ-diphenylamino-tetramethyldialuminum[29] and in the exchange given for the tolylaluminum systems which are similarly reported to go via an intramolecular exchange process.[30] A number of other reports indicate single-bridged intermediates or give rise to exchange processes which may be interpreted in terms of this mechanism.[31-34] The studies of Jeffery and Mole[34] on the mixed-bridged species containing a methyl group and either an oxygen or a nitrogen group clearly follow the same type of rate law with Arrhenius activation energies in the 12–20-kcal/mol range; also, there is no dissociation since no symmetrical products are formed. In some of these instances they reported the surprising observation that alkyl group exchange does not occur in these systems by an intermolecular process—even at elevated (100 °C) temperatures. This is unlike the $(\mu\text{-}CH_3)(\mu\text{-}NPh_2)Al_2(CH_3)_4$ system[29] which undergoes both intramolecular bridge–terminal methyl group exchange and intermolecular exchange or the $(\mu\text{-}CH_3)(\mu\text{-}PhC{\equiv}C)Al_2(CH_3)_4$ system which behaves in a similar manner with both inter- and intramolecular exchange occurring.[32]

These findings strongly suggest that the mechanism for bridge–terminal alkyl exchange may proceed through at least two mechanisms: the first is the mechanism proposed for the self-exchange of trimethylaluminum or of trimethylaluminum with other metal alkyls which involves dissociation and a common intermediate[35,36] while the second mechanism involves an intramolecular process as observed in the cases cited.

In each of these cases at least one of the bridging groups is a strongly bridging ligand which appears to make some processes such as the single-bridge opening mechanism postulated more favorable. This mechanism may be relatively common since many systems have now been prepared in which at least one of the bridge bonds is more stable than that formed by the methyl group and this results in stabilization of the half-bridged species or of some other intramolecular activated complex.

The final process to be described is the averaging process for the nonequivalent terminal methyl groups which is observed both in pentamethylcyclopropylaluminum and in tetramethyldicyclopropylaluminum. Although these processes appear to be the same in both compounds, only that for C, $(\mu\text{-}c\text{-}C_3H_5)_2Al_2(CH_3)_4$, has been studied due to the complexity of the equilibrium systems at hand and the overlap of many of the regions of interest which cause the analysis of the data to be difficult.

The variable-temperature NMR spectra of a sample which contains C "almost exclusively" are shown in Figure 5. The single peak associated with the terminal methyl groups broadens and splits into two well-resolved lines as expected for an exchange process. The kinetic parameters for three samples are shown in Table VI and the Arrhenius activation energy plot is shown in Figure 4. Clearly the precision of the kinetic parameters for this system is not as good as one would like, but it is sufficient to show that the energy of activation for this process is of the order of 11 kcal/mol, substantially less than that observed for the bridge–terminal interchange. Further, the entropy of activation is in the vicinity of zero which would be consistent with an intramolecular rotation process. These processes suggested can be most readily visualized in eq 6 where the bridging cyclopropyl group rotates

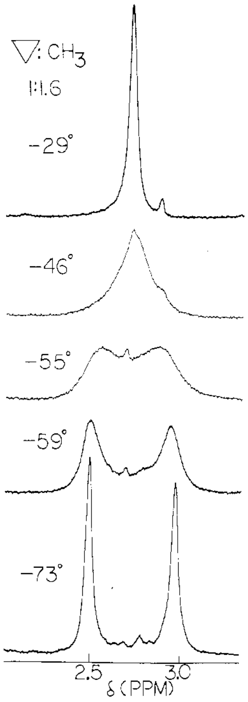
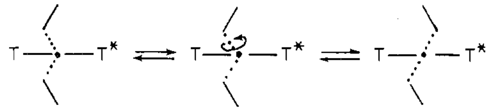


Figure 5. The 60-MHz NMR spectra of the methyl region of a sample containing predominantly tetramethyldicyclopropylaluminum as a function of temperature.

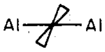
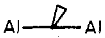
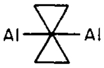


(6)

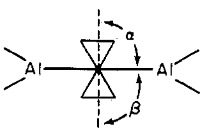
about the axis dropped from the α-carbon atom to the Al–Al axis. Rotation about this axis rapidly on the NMR time scale will lead to magnetic equivalence of the terminal methyl groups. Slowing or stopping this rotation will result in nonequivalence for these sites and lead to the observed low-temperature spectrum.

In order to understand better this rotational process, to estimate the barrier to rotation of the cyclopropyl group, and to determine the minimum energy conformation, CNDO molecular orbital calculations[37] were carried out on dimethylcyclopropylaluminum dimer. The rotational angles of the terminal methyl groups used in the calculation were those which minimized the interactions between the cyclopropyl and methyl hydrogens. The energy of each H–H interaction was estimated from the curve developed by Murrell et al.[38] The energy of the molecule was calculated as a function of the angle of rotation of the cyclopropyl groups, the puckering of the aluminum carbon ring, and the tilting of the cyclopropyl group to reduce the methyl hydrogen–ring hydrogen interactions. The rotational angles α and β are defined as the dihedral angles formed by the plane containing the two aluminum atoms and the α carbon of the bridging cyclopropyl group with the plane formed by the midpoint between the two aluminums, the cyclopropyl α carbon, and the midpoint between the two cyclopropyl β carbons. The degree of puckering is related to γ, the deviation from 90° of the dihedral angle formed by the plane containing all terminal carbons with the plane formed by the two aluminums and a cyclopropyl α carbon. The angle of tilt, δ, is the deviation of the dihedral angle formed by the plane of the cyclopropyl ring and the plane described by the two aluminum atoms and the α carbon of the cyclopropyl ring from the expected angle of 123.1°. These angles are diagrammed in IVa and IVb. For the preliminary calculation, the angles of α and β were chosen to maintain a

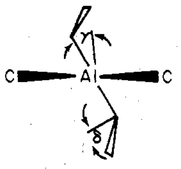
Table VII. CNDO Calculations of the Energy of Various Conformers of Dimethylcyclopropylaluminum Dimer[a]

Rotation angles α–β, deg	Confign	Min energy, kcal/mol	Tilt, deg	Pucker, deg
0–0		−58 506.11	0	0
45–135		−58 511.44	2.5	5
45–225		−58 512.63	0	5
45–315		−58 512.73	0	5
90–90		−58 517.68	0	12.5
90–270		−58 513.13	0	12.5

[a] See IVa and IVb for definition of tilt and pucker and the angles α and β.



IVa top view



IVb view down the Al–Al axis

plane of symmetry in the molecule so that γ and δ were equal for the two cyclopropyl rings. The angles α and β were varied by 45°, γ was varied by 2.5°, and δ was varied by 2.5° to minimize the total energy.

According to these calculations, the most stable conformation is the anti conformation with $\gamma = 12.5°$ and $\delta = 0°$. In this conformation the aluminum–carbon four member ring forms a plane which is inclined to the plane of the four terminal methyl carbons. A local energy minimum 4.5 kcal higher than the ground state was found when β was changed to 270°, the syn conformation. Values for several calculations are collected in Table VII. Angles of 90 or 270° for α and β are expected on a theoretical basis since these conformations may be stabilized by a bonding interaction between the π system of the cyclopropyl rings and the nonbonding d and p orbitals on the aluminums.

A value for γ of 12.5° is consistent with the value of 16° found in the x-ray structure of tricyclopropylaluminum. The configuration with $\alpha = \beta = 0°$, was considered to be one of the highest rotational energy states of the molecule for the rotation of the cyclopropyl groups. Angles of $\gamma = \delta = 0°$ gave the minimum energy for this conformation of 11.5 kcal above the ground state. Similarly holding α at 90° and rotating β from 90 through 270° without minimizing the energy with respect to γ and δ gave a rotational barrier on the order of 11 kcal. Therefore, these calculations are consistent with the mechanism proposed to explain the NMR spectra.

An additional feature which arises from this calculation is a description of the bonding present within the molecule. Some of the data related to this are collected in Table VIII. These indicate substantial metal–metal interaction for all configurations in agreement with the several other calculations which have been performed on bridged aluminum dimers.[39–42] Further, the bonding appears to only vary a small amount with rotation, as anticipated from the small rotational barrier observed and calculated. The most significant changes occur in the 0–0° configuration as shown in Table VII with greater metal–metal interaction occurring at the expense of both Al–C bridge and terminal bonds. This change in bonding is not surprising since this configuration represents the maximum in the rotational process. The bondings in the 90–90° configuration observed in the solid state and in the 90–270° configuration which has the lowest energy as determined from the calculations are very close with regard to the reduced overlap and the orbital participation in bond formation.

Table VIII. Reduced Overlap and Orbital Participation in Formation of the Bonds in Tricyclopropylaluminum Dimer Obtained from CNDO Calculations

Bond	Confign, deg	Reduced overlap	% Al orbitals used			% carbon orbitals used	
			s	p	d	s	p
Al–Al	90–90[a]	0.8377	28.21	41.39	30.41		
	90–270[a]	0.8396	28.24	41.82	30.41		
	0–0[b]	0.8936	27.10	41.83	31.07		
Al–C bridge	90–90[a]	0.7332	15.84	40.58	43.59	45.19	54.81
	90–270[a]	0.7342	15.75	40.57	43.68	45.55	54.45
	0–0[b]	0.7032	15.02	39.10	45.88	44.98	55.02
Al–C terminal	90–90[a]	1.0524	21.01	41.82	37.17	45.59	54.41
	90–270[a]	1.0559	20.68	41.71	37.61	45.32	54.68
	0–0[b]	1.0106	21.38	41.09	37.53	47.03	52.97

[a] Tilt and pucker angles are 0°. [b] Tilt angles is 0° with the pucker equal to 12.5°.

A similar situation seems probable for the bonding and for the rotation of the cyclopropyl group in the pentamethylcyclopropylaluminum dimer which appears to proceed with approximately the same activation parameters as indicated in Figure 4, but no quantitative data for this rotational process were collected on this system due to the equilibria involved which resulted in overlapping peaks in the terminal methyl regions for samples containing this species.

From the studies included in this paper and previous work, we may conclude that there are, at a minimum, three different types of exchange processes which can occur in bridged organoaluminum compounds. These are the dissociation type exchanges observed in the mixed-bridged and strongly bridged systems and finally the rotational process described for the cyclopropyl-bridged systems which occurs in the compounds which have unsymmetrically positioned terminal methyl groups.

Registry No. $Al_2(c\text{-}C_3H_5)_6$, 27072-07-7; $Al_2(CH_3)_6$, 15632-54-9; $(\mu\text{-}CH_3)(\mu\text{-}c\text{-}C_3H_5)Al_2(CH_3)_4$, 58220-13-6; $(\mu\text{-}c\text{-}C_3H_5)_2Al_2(CH_3)_4$, 58220-14-7; $(\mu\text{-}c\text{-}C_3H_5)_2Al_2(c\text{-}C_3H_5)(CH_3)_3$, 58220-15-8; $Hg(c\text{-}C_3H_5)_2$, 13955-96-9; Al, 7429-90-5.

References and Notes

(1) J. P. Oliver and L. G. Stevens, *J. Inorg. Nucl. Chem.*, **21**, 137 (1962).
(2) H. D. Visser and J. P. Oliver, *J. Am. Chem. Soc.*, **90**, 3579 (1968).
(3) G. Zweifel and G. M. Clark, *J. Organomet. Chem.*, **39**, C33 (1972).
(4) C. M. Clark and G. Zweifel, *J. Am. Chem. Soc.*, **93**, 527 (1971).
(5) E. A. Jeffery, T. Mole, and J. K. Saunders, *Aust. J. Chem.*, **21**, 137 (1968).
(6) E. A. Jeffery, T. Mole, and J. K. Saunders, *Chem. Commun.*, 696 (1967).
(7) M. B. Smith, *J. Organomet. Chem.*, **70**, 13 (1974).
(8) J. F. Malone and W. S. McDonald, *J. Chem. Soc., Dalton Trans.*, 2646 (1972).
(9) J. F. Malone and W. S. McDonald, *J. Chem. Soc., Dalton Trans.*, 2649 (1972).
(10) G. D. Stucky, A. M. McPherson, W. E. Rhine, J. J. Eisch, and J. L. Considine, *J. Am. Chem. Soc.*, **96**, 1941 (1974).
(11) J. P. Oliver and D. A. Sanders, *J. Am. Chem. Soc.*, **90**, 5910 (1968).
(12) J. W. Moore, D. A. Sanders, P. A. Scherr, M. D. Glick, and J. P. Oliver, *J. Am. Chem. Soc.*, **93**, 1035 (1971).
(13) G. F. Reynolds, R. E. Dessy, and H. H. Jaffe, *J. Org. Chem.*, **23**, 1217 (1958).
(14) A. L. Van Geet, *Anal. Chem.*, **40**, 2227 (1968).
(15) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance", McGraw-Hill, New York, N.Y., 1959, Chapter 10 and references therein.
(16) K. L. Henold, J. Soulati, and J. P. Oliver, *J. Am. Chem. Soc.*, **91**, 3171 (1969).
(17) J. Müller, K. Margiolis, and K. Dehnicke, *J. Organomet. Chem.*, **46**, 219 (1972).
(18) H. F. Shurvell, *Spectrochim. Acta, Part A*, **23**, 2925 (1967).
(19) A. H. Cowley and T. A. Furtsch, *J. Am. Chem. Soc.*, **91**, 39 (1969).
(20) J. Tanaka and S. R. Smith, *Inorg. Chem.*, **8**, 265 (1969).
(21) R. E. Winters and R. W. Kiser, *J. Organomet. Chem.*, **10**, 7 (1968).
(22) D. B. Chambers, G. E. Coates, F. Glockling, and M. Weston, *J. Chem. Soc. A*, 1712 (1969).
(23) G. Glockling and J. G. Irwin, *J. Chem. Soc., Dalton Trans.*, 1424 (1973).
(24) F. Glockling and R. G. Stafford, *J. Chem. Soc. A*, 1761 (1971).
(25) J. J. Eisch and J. L. Considine, *J. Am. Chem. Soc.*, **90**, 6257 (1968).

(26) P. G. Perkins, Abstracts, 3d International Symposium on Organometallic Chemistry, Munich, 1967, p 348; A. H. Cowley and W. D. White, *J. Am. Chem. Soc.*, **91**, 34 (1969).
(27) P. A. Scherr and J. P. Oliver, *J. Mol. Spectrosc.*, **31**, 109 (1969).
(28) D. C. Poulter, R. S. Boikess, J. I. Brauman, and S. Winstein, *J. Am. Chem. Soc.*, **94**, 2291 (1972).
(29) J. Rie and J. P. Oliver, to be submitted for publication.
(30) T. B. Stanford, Jr., and K. L. Henold, *Inorg. Chem.*, **14**, 2426 (1975).
(31) E. A. Jeffery, T. Mole, and J. K. Saunders, *Aust. J. Chem.*, **21**, 649 (1968).
(32) N. S. Ham, E. A. Jeffery, and T. Mole, *Aust. J. Chem.*, **21**, 2687 (1968).
(33) E. C. Ashby, J. Laemmle, and G. E. Parris, *J. Organomet. Chem.*, **19**, 24 (1969).
(34) E. A. Jeffery and T. Mole, *Aust. J. Chem.*, **23**, 715 (1970).
(35) E. A. Jeffery and T. Mole, *Aust. J. Chem.*, **26**, 739 (1973).
(36) T. L. Brown and L. L. Murrell, *J. Am. Chem. Soc.*, **94**, 378 (1972).
(37) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory", McGraw-Hill, New York, N.Y., 1970.
(38) J. N. Murrell, M. Randic, and D. R. Williams, *Proc. R. Soc. London, Ser. A*, **284**, 566 (1965).
(39) A. H. Cowley and W. D. White, *J. Am. Chem. Soc.*, **91**, 34 (1969).
(40) K. A. Levison and P. G. Perkins, *Theor. Chim Acta*, **17**, 15 (1970).
(41) K. A. Levison and P. G. Perkins, *Discuss. Faraday Soc.*, **47**, 183 (1969).
(42) K. Ohkubo, H. Shimada, and M. Okada, *Bull. Chem. Soc., Jpn.*, **44**, 2025 (1971).

Contribution from Department of Chemistry, McMaster University, Hamilton, Ontario, L85 4M1, Canada, and the Central Research and Development Department, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898

Oxidation States in "$VSbO_4$"

T. BIRCHALL and A. W. SLEIGHT*

Received July 28, 1975 AIC50553C

Antimony Mössbauer studies show that compositions approaching $VSbO_4$ contain Sb only in the pentavalent state. Thus, contrary to earlier proposals, the oxidation states are best represented as $V^{III}Sb^{V}O_4$. Actually, stoichiometric $VSbO_4$ could not be prepared. Phases close to this composition have rutile-related structures, and they can be represented by formulas such as $V_{1-x}Sb_{1-x}O_4(M_{1-x}O_2)$ or $V_{1+y}Sb_{1-y}O_4(MO_2)$.

Introduction

The synthesis of $VSbO_4$ was first reported by Vernon and Milligan.[1] These authors observed a tetragonal rutile-type structure and indicated oxidation states of Sb^{3+} and V^{5+}. Roth and Waring[2] confirmed the rutile-like structure of $VSbO_4$, and they also suggested the existence of a high-temperature polymorph of $VSbO_4$. Schüer and Klemm[3] studied the magnetic properties of $VSbO_4$ and concluded that the oxidation states could not be Sb^{3+} and V^{5+}. However, Schüer and Klemm could not decide between $V^{IV}Sb^{IV}O_4$ and $V^{III}Sb^{V}O_4$. These two possibilities can easily be distinguished by means of ^{121}Sb Mössbauer spectroscopy, and our investigation of this system is reported here.

Experimental Section

The reactants were high-purity Sb_2O_3 and V_2O_5. Gold reaction containers were used since reactions with both platinum and silica were detected. Some preparations were carried out in air; others were in gold tubes which had been evacuated and welded shut.

X-ray powder patterns were obtained at 25 °C with a Hägg–Guinier camera using Cu $K\alpha_1$ radiation and an internal standard of high-purity KCl ($a = 6.2931$ Å). Cell dimensions were refined by least squares.

Mössbauer spectra were recorded on apparatus previously described.[4] Absorbers were prepared by intimately mixing the finely powdered sample with Apiezon grease and placing it between thin aluminum sheets in a copper holder. The samples contained 6 mg of Sb/cm^2. The source $BaSnO_3$ (^{121}Sb) was kept at room temperature (298 K) while the sample temperature was varied.[4] About 150000 counts per folded channel were accumulated using the escape peak from a $Xe-CO_2$ proportional counter. Isomer shifts were measured with respect to InSb at 4 K. Spectra were computer fitted to both a single Lorentzian[5] and an eight-line quadrupole spectrum.[6]

Results

When $VSbO_4$ is prepared in air at 800 °C according to the original synthesis given by Vernon and Milligan,[1] some oxidation occurs. Our analytical data indicate $VSbO_{4.35}$ or, more correctly, $V_{0.92}Sb_{0.92}O_4$. Our tetragonal cell dimensions for this oxidized $VSbO_4$ are given in Table I. Microprobe examination of this product indicates that it is homogeneous.

Table I. Cell Dimensions

a, Å	b, Å	c, Å	Y, deg	V, Å^3	Footnote
4.58		3.06		64.2	*a*
4.598		3.078		65.1	*b*
4.605	4.595	3.065	90.25	64.9	*c*
4.6085	4.6085	3.0839	90.20	65.50	*d*
6.5289	6.5061	3.0839		65.50	*e*
4.6241		3.0369		64.94	*f*

[a] Reference 1; really $V_{1-x}Sb_{1-x}O_2$. [b] Reference 2; really $V_{1+y}Sb_{1-y}O_2$. [c] Reference 3; however, monoclinic cell is changed from second setting to first setting and 3.595 Å is corrected to 4.595 Å. [d] This work; monoclinic cell, $V_{1.05}Sb_{0.95}O_4$. [e] This work; C-centered orthorhombic cell (V/2). [f] This work; $V_{0.92}Sb_{0.92}O_4$.

Preparations in sealed gold tubes did not give single-phase products when the heating temperature was in the range 700–800 °C. The products consisted primarily of a tetragonal rutile-type phase, but there were small amounts of Sb_2O_4 present. This indicates that the formula of the rutile phase was actually $V_{1+y}Sb_{1-y}O_4$ where y is of the order of 0.1. When this sample was quenched from 900 °C, the product appeared to be single phase by x-ray diffraction. However, microprobe studies showed small domains of an antimony oxide. These domains are amorphous. Their composition is not accurately known, but this glassy state may be stabilized by small amounts of vanadium. In any event, the vanadium-to-antimony ratio in the predominate rutile-related phase must be greater than 1. Based on a semiquantitative microprobe analysis, this phase will be referred to as $V_{1.05}Sb_{0.95}O_4$.

Four-probe electrical resistivity data for the very dense quenched product containing $V_{1.05}Sb_{0.95}O_4$ and amorphous antimony oxide showed semiconducting behavior with a room-temperature resistivity of 10^5 ohm-cm and an activation energy of 0.3 eV. These data should be reasonably representative of $V_{1.05}Sb_{0.95}O_4$ since the amorphous inclusions were clearly isolated from one another according to the microprobe studies.

The structure of $V_{1.05}Sb_{0.95}O_4$ quenched from 900 °C is clearly not tetragonal. We find that a C-centered orthorhombic cell will give an excellent account of the diffraction pattern. The cell dimensions are given in Table I, and the indexed pattern is in Table II. In this orthorhombic cell the tetragonal a has been increased by the factor of $2^{1/2}$. A

---

* To whom correspondence should be addressed at Du Pont.