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The Infrared and Raman Spectra of the Trimethylaluminum-Dimethyl Sulfide Complex

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The infrared and Raman spectra of a mixture of trimethylaluminum and dimethyl sulfide (molar ratio, 1 : 1) have been measured (IR: 3100—300 cm^{-1}, Raman: 3100—130 cm^{-1}). The spectra obtained are entirely different from the superposition of the spectra of the two components. Tentative assignments for most of the infrared bands and Raman lines have been suggested. The CS stretching vibration lines of dimethyl sulfide shift to frequencies lower by about 5 cm^{-1} when it is mixed with trimethylaluminum. These findings, together with the measurement of the Raman spectrum of the mixture in a 10-volume-percent benzene solution, indicate that the 1 : 1 mixture of trimethylaluminum and dimethyl sulfide forms a pure coordination complex, $Al(CH_3)_3\cdot(CH_3)_2S$, which does not dissociate into its components appreciably in either the liquid state or the benzene solution.

Dimethyl sulfide forms a coordination complex when mixed with trimethylaluminum. It is known that the Al←S bond in this complex is much weaker than the Al←O bond in the trimethylaluminum - dimethyl ether complex, and that in the vapor phase the trimethylaluminum - dimethyl sulfide complex partially dissociates into trimethylauminum and dimethyl sulfide.[1] To make sure whether, in the liquid state, the mixture of trimethylaluminum and dimethyl sulfide (molar ratio, 1 ; 1) forms a pure coordination complex or whether it contains three chemical species (complex, trimethylaluminum, and dimethyl sulfide) as a result of the partial dissociation, as in the vapor phase, the infrared and Raman spectra of the complex (a 1 : 1 mixture) in the liquid state will be measured. Qualitative polarization data on Raman lines will also be obtained. No infrared or Raman spectrum of any trialkylaluminum - dialkyl sulfide complex has ever been reported, as far as the author is aware.

Experimental

When trimethylaluminum was mixed with dimethyl sulfide in a molar ratio of 1 : 1, considerable heat evolution was observed. Six milliltrters of the mixture was then transferred into a flask, distilled in vacuo into a Raman tube with a volume of 6 ml., and sealed off under reduced pressure. The Raman spectrum was measured in the 3100—130 cm^{-1} region in the liquid state with a Shimadzu GRS Raman spectrophotometer. The polarization data were taken by the use of parallel

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[1] N. Davidson and H. C. Brown, *J. Am. Chem. Soc.*, **64**, 316 (1942).

TABLE I. OBSERVED RAMAN FREQUENCIES OF $(CH_3)_2S$, $Al_2(CH_3)_6$, AND $Al(CH_3)_3 \cdot (CH_3)_2S$ IN cm^{-1} [*1,*2]

$(CH_3)_2S$[*3]			$Al_2(CH_3)_6$[*4]			$Al(CH_3)_3 \cdot (CH_3)_2S$		
						3003	m	D
2980	s	D	2936	m	D	2934	vs	P
2911	vs	P	2892	vs	P	2886	s	P
2832	w	P	2825	w	P	2819	w	P
1609	vw							
						1437	w	D
1426	m	D	1434	w	D	1340	vw	
1325	w	P						
1224	vw		1257	vw	D			
			1203	m	P	1188	m	P
			1137	vw	P	1129	vw	
1041	vw					1031	vw	
						987	vw	
						958	vw	
919	vw					926	vw	
						835	vw	
742	s	D				738	m	D
			722	vw	D	719	vw	D
690	vs	P	685	m	D	685	s	P
						624	m	D
			592	s	P	574	w	D
						521	vs	P
480	vw		495	w	P	465	vw	
			453	s	P			
			311	s	P			
285	s	P				283	w	
						244	vw	
						195	vw	D
						154	s	D
			148	s	D			

[*1] m, medium; s, strong; w, weak; v, very.

[*2] P, polarized; D, depolarized.

[*3] Cited from R. Fonteyne, *J. Chem. Phys.*, **8**, 60 (1940).

[*4] Values listed are obtained by the present author.

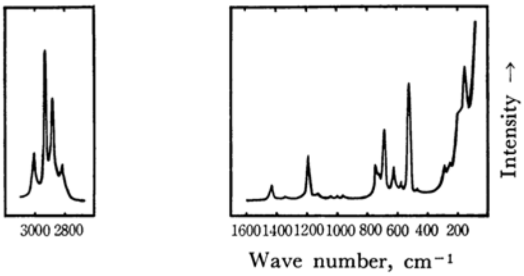

Fig. 1. The Raman spectrum of $Al(CH_3)_3 \cdot (CH_3)_2S$.

and perpendicular Polaroid cylinders placed alternately over the Raman tube. Table I shows the results of these measurements, along with those of trimethylaluminum and dimethyl sulfide. Figure 1 shows the Raman spectrum chart of the trimethylaluminum-dimethyl sulfide complex. The Raman spectrum of the trimethylaluminum - dimethyl sulfide complex was also measured in the 10-volume-percent benzene solution. The infrared spectrum was measured in the 3100—300 cm^{-1} region in the liquid state with a Japan Spectroscopic Co. Model DS-402G infrared spectrophotometer. The procedure described before was used.2)

Results and Discussion

As is shown in Table I, the Raman spectrum of the trimethylaluminum-dimethyl sulfide complex is quite different from the superposition of the spectra of trimethylaluminum and dimethyl sulfide. Not even very strong Raman lines of these components (592 and 311 cm^{-1} lines of trimethylaluminum, 2980 and 2911 cm^{-1} lines of dimethyl sulfide) can be found in the spectrum of the complex.

The principal infrared bands and Raman lines in the 3100—130 cm^{-1} region are tentatively assigned in Table II, taking the assignment for the trimethylaluminum - dimethyl ether complex2,3) and Goggin and Woodward's assignment for the $[CH_3\text{-}Hg\text{-}S(CH_3)_2]^+$ ion4) into consideration. The AlC_3 skeletal vibrations (three AlC_3 stretchings and two AlC_3 deformations) appear at practically the same frequencies, with the same intensities and with the same degree of depolarization (Raman) as in the case of the trimethylaluminum - dimethyl ether complex. Similarly, the CS stretchings, SC_2 scissors, and SC_2 wagging appear at almost the same frequencies as in the case of $[CH_3HgS(CH_3)_2]^+$ ion. Both the CS antisymmetric stretching (742 cm^{-1}) and the CS symmetric stretching vibration line (690 cm^{-1}) of dimethyl sulfide shift to frequencies lower by about 5 cm^{-1} when a complex is formed with trimethylaluminum (Table III). This corresponds closely with the shifts of the CO stretchings of dimethyl ether on forming a complex with trimethylaluminum.2) The magnitudes of shifts are smaller than in the case of $[CH_3HgS(CH_3)_2]^+$.

The Raman spectrum of the trimethylaluminum - dimethyl sulfide complex in the 10-volume-percent benzene solution is merely a superposition of the spectrum of the complex and that of benzene. No line except for the lines of the complex and benzene is found. The positive evidence for the existence of an equilibrium formulated as follows:

$$Al(CH_3)_3 \cdot (CH_3)_2S \rightleftarrows 1/2\ Al_2(CH_3)_6 + (CH_3)_2S,$$

which exists in the vapor phase, is not found in either the liquid state or the benzene solution.

These findings suggest that the 1 : 1 mixture of trimethylaluminum and dimethyl sulfide forms a pure coordination complex, $Al(CH_3)_3 \cdot (CH_3)_2S$, which does not dissociate appreciably into its components in either the liquid state or the benzene solution. It is reasonable to assume that the complex takes a structure similar to that of trimethylaluminum - dimethyl ether complex, in which an unshared pair of electrons of the sulfur atom coordinates to the aluminum atom.

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2) S. Takeda and R. Tarao, This Bulletin, **38**, 1567 (1965).

3) R. Tarao, This Bulletin, 39, 2126 (1966).

4) P. L. Goggin and L. A. Woodward, *Trans. Faraday Soc.*, **58**, 1495 (1962).

TABLE II. OBSERVED FREQUENCIES OF $Al(CH_3)_3 \cdot (CH_3)_2S$ IN cm^{-1} AND VIBRATIONAL ASSIGNMENT*1,*2

IR		Raman			Assignment
2999	w	3003	m	D	CH_3 degenerate str. (SCH_3)
2929	vs	2934	vs	P	CH_3 degenerate str. ($AlCH_3$), CH_3 symmetric str. (SCH_3)
2888	s	2886	s	P	CH_3 symmetric str. ($AlCH_3$)
2860	w				Overtone of CH_3 deform. (SCH_3)
2821	w	2819	w	P	Overtone of CH_3 deform. ($AlCH_3$)
1433	s	1437	w	D	CH_3 degenerate deform. ($AlCH_3$, SCH_3)
1337	vw	1340	vw		CH_3 symmetric deform. (SCH_3)
1312	w				
1256	w				
1185	vs	1188	m	P	CH_3 symmetric deform. ($AlCH_3$)
		1129	vw		
1035	m	1031	vw		CH_3 rock (SCH_3)
984	m	987	vw		
949	vw	958	vw		
916	vw	926	vw		
851	vw	835	vw		
		738	m	D	CS antisymmetric str. A
716	vs	719	vw	D	AlC_3 degenerate str. A'', CH_3 rock ($AlCH_3$)
678	s	685	s	P	CS symmetric str. A'
623	m	624	m	D	AlC_3 degenerate str. A'
		574	w	D	
521	s	521	vs	P	AlC_3 symmetric str. A'
457	vw	465	vw		
437	w				
287	w	283	w		SC_2 scissors A'
		244	vw		AlC_3 symmetric deform. A'
		195	vw	D	SC_2 wag A'
		154	s	D	AlC_3 degenerate deform. A''

*1 m, medium; s, strong; w, weak; v, very.

*2 P, polarized; D, depolarized.

TABLE III. SHIFTS OF THE C-S VIBRATION LINES ON COMPLEX FORMATION

	ν_{as}(CS) (cm^{-1})			ν_s(CS) (cm^{-1})		
$(CH_3)_2S$*1	742	s	D	690	vs	P
$Al(CH_3)_3 \cdot (CH_3)_2S$	738	m	D	685	s	P
$CH_3Hg\text{-}S(CH_3)_2{}^{+}$*2	729	mw	D	675	m	P

*1 Cited from R. Fonteyne, loc. cit.

*2 Cited from P. L. Goggin and L. A. Woodward, Ref. 4.

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