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Raman Spectra of Arsenic Trichloride in Water and Alcohols and the Spectrum of Arsenic Tribromide[1]

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Received July 26, 1968

Liquid $AsCl_3$ and its solutions in a number of solvents [H_2O, D_2O, CH_3OH, C_2H_5OH, $CH_3CHOHCH_3$, $(CH_3CH_2)_2O$] have been investigated with Raman spectroscopy. Although the stretching frequencies of $AsCl_3$ are strongly affected by all solvents except diethyl ether, the Raman spectra can be interpreted as being consistent with a pyramidal structure of C_{3v} symmetry. New lines were observed at 710 cm^{-1} in H_2O solution, at 690 cm^{-1} in D_2O, and between 620 and 660 cm^{-1} in alcohols, along with a lower frequency line at *ca.* 240 cm^{-1} in all of these solutions. These data are interpreted as indicative of the formation of aquo and alcohol complexes with $AsCl_3$. There is little evidence for the loss of Cl^- or formation of As(III) species with fewer than three chlorides until As_4O_6 is precipitated upon complete hydrolysis. A species H_2OAsCl_3 is believed in equilibrium with $HOAsCl_3^-$ because the intensity of the 710-cm^{-1} line increases upon dilution with H_2O and this equilibrium is reversed with acid concentrations of *ca.* 3 *M*. Finally, the Raman spectrum of $AsBr_3$(l) has been reinvestigated. The existence of four Raman lines is demonstrated with their proper polarizations for C_{3v} symmetry. The assignments given are: ν_1 (A_1) 272 ± 3 cm^{-1}, polarized; ν_3 (E) 287 ± 3 cm^{-1}, depolarized; ν_2 (A_1) 130 ± 1 cm^{-1}, polarized; ν_4 (E) 100 ± 1 cm^{-1}, depolarized. In ether solution, the positions of ν_1 and ν_3 are reversed.

Introduction

The structural characterization of liquid $AsCl_3$ from Raman spectra has been shown previously by a number of workers.[2-8] Its pyramidal shape is well supported. Investigations of $AsCl_3$ in solvents, however, are neither as well documented nor are results as well agreed upon. Kato and Someno[9] and Finkelstein[10] found no Raman spectral changes in diethyl ether solution. In methanol, ethanol, and 2-propanol solutions, Sack and Brodskij[11] observed both a broadening and a lowering of the stretching frequencies of $AsCl_3$, which they interpreted as molecular deformations; however, they found no new Raman lines. Such behavior was not observed in CCl_4, C_6H_6, or ether. In 1920, Marquis[12] determined from conductivity measurements that in ethanol $AsCl_3$ forms an addition product. Addition of dry C_2H_5OH to $AsCl_3$ caused an *increase* in resistance; if solvolytic action had taken place, the resistance should have *decreased.* Several authors[13-15] have found evidence of arsenic trichloride-ether adducts, contrary to Raman spectroscopic investigations.[9,10]

The limited solubility of $AsCl_3$ in water as a solvent was observed by Penny and Wallace,[16] but no other investigation of this system appears to have been made. The presence of negatively charged chloro complexes of $AsCl_3$ has been postulated, as in the ion-exchange study of Nelson and Kraus,[17] an isotopic-exchange study by Lewis and Sowerby,[18] or the solubility studies of a variety of compounds by Gutmann[19] in liquid $AsCl_3$. Arcand[20] has proposed mixed hydroxochloro species (*e.g.*, $AsCl_2OH$) with coordination number 3, as well as species with lower coordination numbers in aqueous solution. Also, Garrett, *et al.*,[21] in analyzing the solubility behavior of As_4O_6 in HCl, postulated the formation of the oxychloride and the hydroxydichloride, but independent evidence for such species does not exist.

Salt or complex formation of $AsCl_3$ with alkali metal chlorides or organic amine hydrochlorides was discussed by Petzold[22] and Gutmann,[19] but all compounds were observed to be rapidly decomposed by water or alcohol, and only elemental analyses were obtainable. According to such studies, however, As(III) should exhibit coordination numbers as high as 6 with chloride, as in $(C_5H_6N)_3[AsCl_6]$.[23] A Raman study by Delwaulle and Schilling[24] with mixtures of $AsCl_3$ and $AsBr_3$ was interpreted as showing mixed trihalides maintaining a coordination number of 3. Thus with excess $AsCl_3$ and some added $AsBr_3$, a new spectrum appeared which was not a simple superposition of the individual trihalide spectra and indicated $AsCl_2Br$. Similarly, $AsClBr_2$ was demonstrated.

The most recent Raman spectral data on $AsBr_3$(l) have come from the work of Miller and Baer[25] in which the peculiarities of the spectrum were questioned although not satisfactorily solved. Previous work-

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[1] Supported by a research grant from the Office of Saline Water, U. S. Department of the Interior.

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[6] D. M. Yost and J. E. Sherborne, *J. Chem. Phys.*, **2**, 125 (1934).

[7] D. M. Yost and T. F. Anderson, *ibid.*, **3**, 754 (1935).

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[11] A. M. Sack and A. I. Brodskij, *ibid.*, **2**, 215 (1935); *Zh. Fiz. Khim.*, **10**, 866 (1937).

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[13] F. I. Terpugov, *Zh. Obshch. Khim.*, **2**, 868 (1932).

[14] M. Usanovič, *ibid.*, **5**, 996 (1935).

[15] V. S. Finkelstein and P. Kurnosova, *Zh. Fr. Khim.*, **6**, 1232 (1935).

[16] F. Penny and W. Wallace, *Phil. Mag.*, **4**, 361 (1852).

[17] F. Nelson and K. A. Kraus, *J. Am. Chem. Soc.*, **77**, 4508 (1955).

[18] J. Lewis and D. B. Sowerby, *J. Chem. Soc.*, 336 (1957).

[19] V. Gutmann, *Z. Anorg. Allgem. Chem.*, **266**, 331 (1951).

[20] G. M. Arcand, *J. Am. Chem. Soc.*, **79**, 1865 (1957).

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[22] W. Petzold, *Z. Anorg. Allgem. Chem.*, **214**, 355 (1933).

[23] L. F. Audrieth, A. Long, and R. E. Edwards, *J. Am. Chem. Soc.*, **58**, 428 (1936).

[24] M. Delwaulle and G. Schilling, *Compt. Rend.*, **244**, 70 (1957).

[25] F. A. Miller and W. K. Baer, *Spectrochim. Acta*, **17**, 112 (1961).

ers[5,9,26] had reported either too many or too few spectral lines to make complete assignments. Aqueous solution chemistry of $AsBr_3$ is lacking since the compound is readily hydrolyzed to As_4O_6.[27,28] Raman spectra of $AsBr_3$ in ether solution have been reported by Finkelstein and Kurnosova[15] and Kato and Someno.[9] These authors argued against complex formation, whereas Usanovič,[29] from conductance measurements, postulated a 1:1 adduct. Again, as with the chlorides, some solid compounds have been reported[30] with coordination numbers 4, 4.5, 5, and even 6. Petzold[22] has prepared compounds with analyses corresponding to the complex anion formulas $AsBr_4^-$ and $As_2Br_7^-$. However, as with chlorides, the bromo-complex compounds are decomposed in most solvents.

In this study, the effect of solvents, especially water, on the structure of $AsCl_3$ is investigated by Raman spectroscopy. This represents also a logical extension of previous work in which the hydrolysis products of As_4O_6 in water were identified.[31] Especially owing to the rapid hydrolysis and also the limited solubility range of $AsCl_3$ in H_2O, the present study *via* spectroscopic means is particularly suitable to detect and identify solution species.

Experimental Section

Apparatus.—Raman spectra were obtained on a Cary Model 81 recording spectrometer with a low-pressure mercury vapor arc as an exciting source. The 4358-Å line was used to obtain most spectra, but the spectrum of the yellow $AsBr_3$ melt was recorded by isolating the 5461-Å (green) Hg line. This exciting line was selected from the mercury lamp by surrounding the sample with a green filter solution prepared from a mixture of $CuSO_4$, $Cu(NO_3)_2$, $K_2Cr_2O_7$, and Pr_2O_3 in water with a maximum transmittance of *ca.* 40% at 546 mμ. Solutions were placed in 7-ml sample tubes of Pyrex glass surrounded by a Wratten 2A gelatin filter (Eastman Kodak Co.) to absorb the mercury continuum. Polarization of spectral lines was determined by the method of Edsall and Wilson[32] using calibrated[33] polaroid sheets (Bausch and Lomb). Solutions in diethyl ether were not surrounded by any filters to prevent boil-off of solvent, the ambient lamp compartment temperature being *ca.* 40°. A Perkin-Elmer Model 521 grating infrared spectrophotometer was used to record parts of the spectrum of $AsBr_3$(l) in a molded polyethylene cell of 0.1-mm path length (Barnes Engineering, Stamford, Conn.). Reported frequencies are accurate to ±3 cm^{-1}.

Sample Preparation.—All solutions were prepared from analytical reagent grade chemicals used without further purification. Liquid $AsCl_3$ was obtained from the General Chemical Division of the Allied Chemical Corp. (Baker and Adamson). It is infinitely soluble in methanol, ethanol, 2-propanol, or diethyl ether, but has a limited solubility range in water. It is immiscible with small amounts of water (<10 mol of H_2O to 1 mol of $AsCl_3$) but precipitates as As_4O_6 in excess water (>20 mol of H_2O to 1 mol of $AsCl_3$). The aqueous solutions of $AsCl_3$ were prepared by rapid stirring in small beakers with the slow addition of water to a measured amount of $AsCl_3$ liquid; organic solvents could be simply added in the desired quantity to measured volumes or weights of $AsCl_3$. D_2O employed was assayed at 99.7%. The $AsBr_3$ was purchased from Alfa Inorganics, Inc. It is nearly colorless as the solid but turned pale yellow on melting. The liquid was added to prewarmed sample tubes and remained liquid in the lamp compartment of the spectrometer. Solid $AsBr_3$ is readily soluble in ether solution. Solid derivatives of $AsCl_3$ were prepared according to reports in the literature.[19,22] Analysis for As(III) followed the method of Vogel,[34] and Cl^- was determined as AgCl by gravimetric methods. *Anal.* Calcd for $(CH_3)_4NAsCl_4$: As, 25.76; Cl, 48.75. Found: As, 26.46; Cl, 46.45.

Results

$AsCl_3$.—The Raman spectrum of pure, liquid $AsCl_3$ observed with photoelectric recording, as opposed to earlier photographic work, is given in Table I and Figure 1.

TABLE I

RAMAN SPECTRUM OF $AsCl_3$(l) (C_{3v} SYMMETRY)

Freq, ±2 cm^{-1}	Polarization	Assignment
411	p	ν_1 (A_1)
380	dp	ν_3 (E)
195	p	ν_2 (A_1)
159	dp	ν_4 (E)

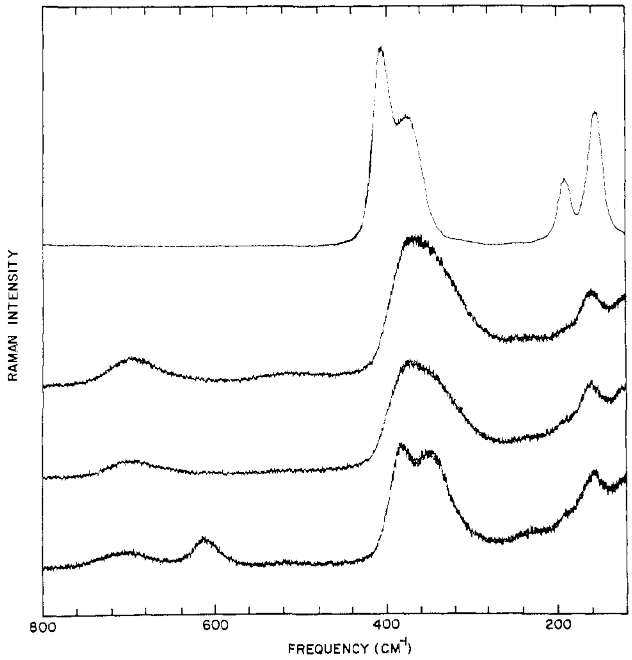

Figure 1.—From top to bottom: (1) Raman spectrum of $AsCl_3$(l), RD 3, slit width 10 cm^{-1}, sensitivity 1.6 × 50; (2) spectrum of 1:10 $AsCl_3$–H_2O; (3) spectrum of $AsCl_3$ in 6 *M* HCl, RD 4, slit width 10 cm^{-1}, sensitivity 1.4 × 100; (4) spectrum of $AsCl_3$ in 1:1 CH_3OH–H_2O, RD 4, slit width 10 cm^{-1}, sensitivity 1.6 × 100.

In an equal-volume mixture of $AsCl_3$ with dry methanol, the two stretching frequencies, ν_1 and ν_3, were lowered to 398 and 352, respectively, whereas the two bending modes appeared to be unaffected.[11] In addition, two new Raman lines were observed: one at 618 cm^{-1} was polarized and a weak line at 240 cm^{-1} was depolarized. In solutions of $AsCl_3$ in ethanol, the As–Cl stretching and bending modes appeared as in the

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(26) O. Redlich, T. Kurz, and W. Stricks, *Monatsh.*, **71**, 1 (1937).

(27) G. S. Serullas, *Ann. Chim. Phys.*, **38**, 318 (1828).

(28) J. Nickles, *J. Pharm. Chim.*, **41**, 142 (1862).

(29) M. Usanovič, *Zh. Fiz. Khim.*, **6**, 923 (1935).

(30) P. Popov, *Zh. Obshch. Khim.*, **9**, 1265 (1939); *ibid.*, **19**, 47 (1949).

(31) T. M. Loehr and R. A. Plane, *Inorg. Chem.*, **7**, 1708 (1968).

(32) J. T. Edsall and E. B. Wilson, *J. Chem. Phys.*, **6**, 124 (1938).

(33) D. H. Rank and R. E. Kagarise, *J. Opt. Soc. Am.*, **37**, 798 (1947); **40**, 89 (1950).

(34) A. I. Vogel, "Quantitative Inorganic Analysis," John Wiley & Sons, Inc., New York, N. Y., 1961, p 376.

CH_3OH solution, but with a new line at 660 cm^{-1}, and in 2-propanol at 622 cm^{-1}; both C_2H_5OH and 2-C_3H_7OH solutions showed the weak 240-cm^{-1} line. No new lines, however, could be detected for $AsCl_3$ dissolved in ether solution; in fact, resolution between ν_1 and ν_3 was somewhat clearer than in pure $AsCl_3$(l).

$AsCl_3$ becomes miscible with water at a ratio of 1 mol of $AsCl_3$ to *ca.* 10 mol of H_2O (hereafter abbreviated 1:10 $AsCl_3$–H_2O), but As_4O_6 settles out owing to hydrolysis when this ratio exceeds *ca.* 1:200. As_4O_6, as the precipitate, was identified by its Raman spectrum. The supernatant solution above this precipitate gave a Raman spectrum identical with that of a saturated solution of As_4O_6 in H_2O, *i.e.*, owing to the presence of the soluble species $As(OH)_3$,[31] and showed no indication of any As–Cl frequencies.

The Raman spectrum of 1:10 $AsCl_3$–H_2O is shown in Figure 1. The most striking feature is that the As–Cl stretching bands have coalesced into a single broad band with an apparent maximum at 375 cm^{-1}, considerably lower than in the pure liquid or the alcohol solutions. In addition, the bending modes of $AsCl_3$ are seen at 195 and 165 cm^{-1}, very close to their original frequencies. Finally, new lines at 710, 525, and 240 cm^{-1} have been observed, as shown. Polarization studies have indicated that the 710-cm^{-1} line, the 525-cm^{-1} line, the higher frequency component of the 375-cm^{-1} band, and the 195-cm^{-1} line are all polarized Raman lines, whereas the remaining three lines, *i.e.*, the lower frequency component of the 375-cm^{-1} band and the 240- and 165-cm^{-1} lines, are depolarized. In D_2O solution, the spectrum was identical with that above except that the 710-cm^{-1} line was lowered in position to *ca.* 693 cm^{-1}.

On further addition of H_2O to the 1:10 $AsCl_3$–H_2O solution, but prior to precipitation of As_4O_6, the 375-cm^{-1} band was observed to shift to still lower frequency, maximizing at its lowest position of *ca.* 350 cm^{-1}. The intensities of the 350-cm^{-1} band as well as the 190- and 160-cm^{-1} regions are decreased considerably whereas the intensities of the *new* lines at 710, 525, and 240 cm^{-1} remain nearly constant, compared to the 1:10 $AsCl_3$–H_2O spectrum (Table II). The polarizations remained as in the preceding case.

TABLE II

INTEGRATED INTENSITIES (NORMALIZED TO 1 *M* $AsCl_3$) OF SELECTED RAMAN BANDS BEFORE AND AFTER DILUTION WITH H_2O

	1:10 $AsCl_3$–H_2O ([As(III)] = 3.5 *M*)	1:15 $AsCl_3$–H_2O ([As(III)] = 2.5 *M*)	% change
375-cm^{-1} band[a]	240	150	−38
525-cm^{-1} line	7	8	+14
710-cm^{-1} line	40	50	+25

[a] About 350 cm^{-1} after dilution.

When, instead of H_2O, either 3 or 6 *M* HCl solutions were used to solvate $AsCl_3$, the Raman spectra appeared qualitatively the same as the 1:10 $AsCl_3$–H_2O spectrum with a 375-cm^{-1} band maximum (Figure 1). Any further dilution with either HCl solution caused no changes in band shapes or peak positions, but all of the Raman lines not characteristically due to $AsCl_3$ (*i.e.*, the 710-, 525-, and 240-cm^{-1} lines) are lower in intensity compared to the H_2O solutions of corresponding $AsCl_3$ concentrations. This intensity change was more pronounced in the 6 *M* HCl than in the 3 *M* HCl addition.

Spectra obtained after the addition of saturated NaCl solution to 1:10 $AsCl_3$–H_2O showed a frequency shift of the 375-cm^{-1} band to 350 cm^{-1}. Hence, the addition of either H_2O or the saturated NaCl solution produced identical spectral results, whereas addition of a 4.6 *M* $HClO_4$ solution produced no such spectral shift.

The spectrum of $AsCl_3$ was also recorded in a mixed solvent composed of methanol and water (Figure 1). The composition of the mixed solvent (*ca.* 1:1 mol ratio) was so chosen as to produce an activity of water[35] approximately equal to that in a 6 *M* HCl solution.[36] The band positions of the As–Cl stretching and bending modes correspond closely to the 6 *M* HCl solution of $AsCl_3$, although better resolution is seen in the stretching region. Furthermore, both a 710- and a 618-cm^{-1} line are observed along with a weak line at 240 cm^{-1}. The 710-, 618-, and 380-cm^{-1} Raman lines are all polarized whereas the others are depolarized. The spectral features of the various $AsCl_3$ solutions are summarized in Table III.

TABLE III

RAMAN FREQUENCIES OF SOLUTIONS OF $AsCl_3$[a]

$AsCl_3$(l)	$AsCl_3$ in CH_3OH	$AsCl_3$ in C_2H_5OH	$AsCl_3$ in $(C_2H_5)_2O$	$AsCl_3$ in 1:1 CH_3OH–H_2O
				710 p
	618 p	660 p		618 p
411 p	398 p	395 p	411 p	380 p
380 dp	352 dp	348 dp	380 dp	345 dp
	240 dp	240 dp		240 dp
195 p	194 p	194 p	195 p	~160 asym, b
159 dp	159 dp	160 dp	159 dp	

1:10 $AsCl_3$–H_2O	~1:15 $AsCl_3$–H_2O	$AsCl_3$ in 3 *M* HCl	$AsCl_3$ in 6 *M* HCl	$AsCl_3$ in aq NaCl	$AsCl_3$ in 4.6 *M* $HClO_4$	1:10 $AsCl_3$–D_2O
710 p	710 p	710 p	710 p, w	710 p	710 p	693 p
525 p, w	525 p, w	525 p, vw	...	525 p	ClO_4^- lines	525 p
375[b]	350[b]	375[b]	375[b]	350[b]	375[b]	375[b]
240 dp	240 dp	240 dp	...	240 dp	240 dp	240 dp
195 p, w	195 vw	195 p	195 p	195 vw	195	195 p
165 dp	165 dp	160 dp	160 dp	165 dp	165 dp	165 dp

[a] Abbreviations: p, polarized; dp, depolarized; v, very; w, weak; b, broad. [b] Apparent band maximum of two Raman lines of which the higher frequency component is polarized and the lower frequency component is depolarized.

Solid Derivatives.—Solutions of $AsCl_3$ saturated with HCl(g) (1 atm) showed no changes in the spectrum. However, white crystalline solids prepared from $(CH_3)_4NCl$ or $C_5H_5N \cdot HCl$ and equimolar $AsCl_3$ showed rather different results. Analysis of the tetramethylammonium derivative indicated $Cl^-/As(III) \approx 4$; its Raman spectrum showed lines at 397 s, 378 m, 358 m, 328 s, 215 w, 195 w, and 165 m cm^{-1} whereas that of the pyridinium hydrochloride showed lines at 384 s, 357 vs,

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(35) W. S. Brown and D. S. Martin, U. S. Atomic Energy Commission Report ISC-235 (1951).

(36) E. W. Washburn, Ed., "International Critical Tables," Vol. VII, McGraw-Hill Book Co., Inc., New York, N. Y., 1930, p 233.

b, 327 m, 278 s, vb, asym, ~190 w, ~175 m, and 160 w cm^{-1}. Because polarized Raman measurements cannot be made with polycrystalline samples and because single-crystal spectra were not measured, it is not possible to decide whether the chloroarsenic moiety in these solids is tetrahedral. It is important to note, however, that the spectra are different from any of those obtained in solution. Both NH_4Cl and KCl (saturated aqueous solutions) gave white precipitates with $AsCl_3$. No satisfactory Raman spectra could be obtained from these salts. Qualitative analysis, however, showed the presence of both As(III) and Cl^- in these derivatives.

$AsBr_3$.—The Raman spectrum of $AsBr_3$ (melt) excited by the 5461-Å Hg line is shown in Figure 2. It is apparent that the 130-cm^{-1} line is polarized and the 100-cm^{-1} line is depolarized. The 274-cm^{-1} band clearly shows accentuated asymmetry on going from perpendicular to parallel polaroid filter orientations indicating the presence of two lines in this region of which one is polarized. Similar conclusions are drawn from analyzing the band with an analog computer. The Raman spectrum of $AsBr_3$ was also investigated in a diethyl ether solution. Its spectrum showed a striking change in band contour in the stretching region, although no frequency shift could be detected for the low-frequency bending modes (compared to the liquid) (cm^{-1}): ν_1 (A_1) 287 p; ν_3 (E) 270 dp; ν_2 (A_1) 130 p; ν_4 (E) 100 dp. The asymmetry of the stretching region band was clearly observed to the lower frequency side for the ether solution in contrast to Figure 2.

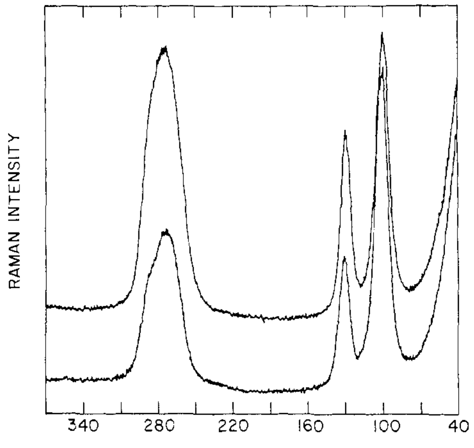

Figure 2.—Raman spectrum of molten $AsBr_3$ excited by the 5461-Å Hg line: upper trace, incident polarization perpendicular to the sample tube; lower trace, polarization parallel to the sample tube.

In the infrared spectrum, the $AsBr_3$ melt indicated a weak line at 374 cm^{-1} and a medium intense line at 556 cm^{-1} (the very weak polyethylene line at *ca.* 550 cm^{-1} has been taken into account; there is no intensity enhancement of other polyethylene lines in the presence of sample). The infrared instrument could not be used for the study of the low-lying fundamental modes of $AsBr_3$.

Discussion

$AsCl_3$.—The pyramidal structure of $AsCl_3$ is well established. It belongs to the C_{3v} point group and all of its fundamental vibrational modes are Raman active: $2A_1$ and 2E modes. The spectral results as given in Table I agree well with published values,[2-8] although the position of ν_3 has generally been most uncertain. In alcoholic solutions, the fundamentals are slightly affected but two new lines are observed of which one is polarized and one is depolarized. In ether no new lines are observed. Since the fundamentals are essentially unaltered in frequencies, relative intensities, and polarization, the spectra suggest that the pyramidal (C_{3v}) symmetry is maintained, yet an alcohol–$AsCl_3$ interaction has occurred as indicated by the presence of new spectral lines. The line position between 600 and 700 cm^{-1} is characteristic of an As–OH interaction.[31,37] In an aqueous solution such a line was seen at 710 cm^{-1} and exihibits an isotope effect. Clearly this may be assigned to an As–OH interaction; in ether, lacking an OH group, no such interaction was observed. The spectra of alcoholic $AsCl_3$ solutions are thus consistent with a "five-atom" pyramidal model of C_{3v} symmetry. Such a species would give rise to an irreducible representation, $\Gamma = 4A_1 + A_2 + 5E$, of which one A_1, the A_2, and two E modes belong to nonvibrational degrees of freedom. Thus, the nine normal vibrational modes are given by $3A_1 + 3E$, as is observed. The "fifth atom" has to be considered as ROH, positioned along the threefold rotation axis of $AsCl_3$. The experiments support the conclusions that the As–Cl vibrational modes are relatively little affected by the nature of R, yet it is necessary that an OH donor is present for binding with the solvent molecules.

The interaction of water with $AsCl_3$ is clearly more pronounced as evidenced by its peculiar solubility behavior and subsequent hydrolysis to As_4O_6(s). The solution Raman spectra similarly support this view. New spectral lines are observed (710, 525, 240 cm^{-1}) and the $AsCl_3$ fundamentals are shifted more severely than in the alcoholic solutions. It is noteworthy, however, that the trends established on solvating $AsCl_3$(l) in alcohol are continued: (1) new spectral lines characteristic of As–OH bond formation, (2) a lowering of the As–Cl stretching frequencies, and (3) a broadening of the spectral envelope. A loss of Cl^- ion from $AsCl_3$ due to solvolysis and the subsequent formation of molecular species with fewer than three chlorides per arsenic should give rise to As–Cl stretching frequencies that lie higher than those observed in the 375-cm^{-1} band. Furthermore, the existence of $As(OH)_3$ is ruled out since the 710-cm^{-1} line is not accompanied by a lower frequency shoulder at 655 cm^{-1}, as was established in earlier work.[31] The experiments in D_2O, moreover, illustrate that only the 700-cm^{-1} region is

(37) R. R. Shagidullin and T. E. Pavlova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 995 (1965); 2091 (1966).

sensitive to this solvent change whereas the other spectral lines show no isotope effect and cannot involve As–OH vibrational motion.

Further dilution of the 1:10 $AsCl_3$–H_2O solution showed accompanying spectral changes, especially in the As–Cl frequencies and intensities. It was demonstrated by experiment, however, that this frequency shift occurs only in "nonacidic" medium; *i.e.*, the shift from 375 to 350 cm^{-1} was *not* observed either in 3 or 6 *M* HCl or in ∼5 *M* $HClO_4$ but was seen clearly in H_2O or NaCl solutions. This suggests that $[H^+]$ plays a more critical role than $[Cl^-]$. In proposing the existence of distinct H_2OAsCl_3 species, as for the analogous alcohol solutions, three additional facts must be rationalized to account for the observed Raman spectrum in terms of a "five-atom" model: (1) The frequency maximum in the As–Cl region shifts from 375 to 350 cm^{-1} on dilution. (2) What is the nature of the line observed at 525 cm^{-1}, since the model allows only for six Raman lines? (3) The intensities of the 710-, 525-, and 240-cm^{-1} lines increase relative to the As–Cl vibrational mode intensities on dilution (Table II).

The shift in frequency was *not* observed in solutions of high $[H^+]$. It is plausible that the high $[H^+]$ represses the ionization of $AsCl_3$-bound water molecules. Formation of $AsCl_3 \cdot OH^-$ necessarily introduces negative charge into the molecule which is a sufficient reason to cause a frequency shift of the magnitude observed, *while also enhancing the intensity of the As-bound OH*. However, the loss in intensity in the As–Cl stretching region is accompanied by an intensity increase in both of the higher frequency lines of a slightly different magnitude. It appears plausible that there is formation of minor concentrations of species with fewer than three Cl^- per As(III) atom. It seems likely that replacement of one or two Cl^- by OH^- should precede formation of $As(OH)_3$ as occurred on further addition of H_2O. Thus, it is suggested that the polarized 525-cm^{-1} line observed in these solutions represents the As–Cl stretching motion of such minor species with fewer than three Cl^- per As(III) atom. Species such as $AsCl_2OH$ have been postulated[20] although no rigorous proof of their existence is available. An equilibrium between two major species

$$\underset{\text{I}}{Cl_3AsOH_2} + H_2O \rightleftharpoons \underset{\text{II}}{Cl_3AsOH^-} + H_3O^+$$

appears reasonable. It is affected by $[H^+]$, not $[Cl^-]$. Both species I and II show a 710-cm^- line due to bound OH but the frequency maximum of the As–Cl stretching vibrations is lowered from 375 cm^{-1} in I to 350 cm^{-1} in II.

$AsBr_3$.—A large series of group V trihalides is known, and, generally, these show C_{3v} symmetry. It was peculiar that a recently published[25] Raman spectrum of $AsBr_3$(l) did not conform to the expected $2A_1 + 2E$ pattern, especially since no *polarized* lines were observed. Recent X-ray structure determinations prove $AsBr_3$ to consist of discrete pyramidal molecules both in the crystalline form[38] and in the liquid.[39] The present investigation (Figure 2) removes these anomalous findings. The relative positions[40–43] of ν_1 (A_1) and ν_3 (E) are quite sensitive to the mass of the halogen atoms bonded to the group V atom as is shown in Table IV. Among the phosphorus trihalides, the correlation between the frequencies of ν_1 and ν_3 and the masses of the bonded halogen atoms is quite clear. In the case of the arsenic trihalides, however, experimental results for these frequencies differ widely enough such that this correlation appears ambiguous. Manley and Williams,[43] for example, from recent infrared investigations have assigned startlingly different values for AsI_3 compared to those of Stammreich, *et al.*[42] However, for $AsBr_3$ their assignments were based on infrared spectra of a dispersion of $AsBr_3$ in Epolene film, whereas the frequency assignments in this work are taken from polarization measurements of the Raman spectrum of liquid $AsBr_3$. It is interesting that the frequency of ν_1 *calculated* by Manley and Williams *is* lower than that of ν_3.

TABLE IV
STRETCHING FREQUENCIES (CM^{-1}) FOR SOME GROUP V TRIHALIDES

Compd	ν_1 (A_1)	ν_3 (E)	Ref
PCl_3	507	494	40, 41
PBr_3	392	392	40
PI_3	303	325	42
$AsCl_3$	411	380	This work
$AsBr_3$	272	287	This work
	279	272	43
AsI_3	216	221	42
	226	201	43

The Raman spectrum of $AsBr_3$ in ether solution showed no new lines, as with $AsCl_3$ in ether; however, the positions of ν_1 and ν_3 appeared to have been reversed as shown by the band asymmetry. In $AsBr_3$(l), the asymmetry in the ν_1–ν_3 band contour lies to the higher frequency side whereas in the ether solution the asymmetry lies on the low-frequency side. The apparent maximum shifted from 287 to 281 cm^{-1} on interchanging the polarizing filter, in support of assigning the ν_1 (A_1) in ether solution at the higher frequency. It seems unlikely that depolymerization is the cause of this frequency reversal since $AsBr_3$ is not associated in the liquid according to the X-ray data available.[39]

The Miller and Baer[25] assignments were in part based on combination bands of $AsBr_3$. These authors had found a combination band at 382 cm^{-1} in the Raman spectrum which was assigned as $\nu_1 + \nu_4$, although ν_1 was not observed. Attempts to find this weak Raman line failed; however, under high instrument sensitivity conditions, two very weak, but reproducible, bands were located at 362 and 410 cm^{-1}. In the infrared spectrum, molten $AsBr_3$ showed a medium-inten-

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[42] H. Stammreich, R. Forneris, and Y. Travares, *J. Chem. Phys.*, **25**, 580 (1956).
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sity line at 556 cm^{-1} and a weaker line at 374 cm^{-1}. Since the polyethylene sample holder has a broad absorption between 600 and 900 cm^{-1} in the ir spectrum, the 650-cm^{-1} line reported by Miller and Baer could not be confirmed. Studies of $AsBr_3$ in H_2O could not be carried out since it is hydrolyzed much more readily than $AsCl_3$ and failed to show any solubility.

Two papers by Davies and Long[44] appeared subsequent to the conclusion of this study which show infrared and Raman evidence for $AsCl_3$ complexes in tri-*n*-butyl phosphate and chloro complexes in ether extracts of $AsCl_3$–HCl. It is interesting to note the absence of any As—O vibrational lines in the tributyl phosphate whereas the P═O frequency was shown to be quite sensitive. The depolarized Raman line observed by us near 345 cm^{-1} in alcohol solution accompanies the polarized line near 390 cm^{-1} and is not necessarily analogous to the line observed in tributyl phosphate by these authors. The existence of tetrachloroarsenites in ether extracts is significant since species with similar spectra are not found in aqueous medium and so tetrachloroarsenites cannot be present in water in appreciable concentration. The line reported by Davies and Long at 740 cm^{-1} in ether extracts from aqueous hydrochloric acid solution may represent an As–O vibration rather than an overtone of a line observed at 383 cm^{-1}. The assignment of the liquid $AsBr_3$ spectrum[44] differs slightly from ours in that, although we agree that there are overlapping bands at 272 and 287 cm^{-1}, we differ as to which is polarized and hence which is ν_1. Our assignment is based on analysis of Figure 2 by methods outlined above. Such analysis could not be performed on the spectrum reported by Davies and Long.

[44] J. E. D. Davies and D. A. Long, *J. Chem. Soc.*, *A*, 1757, 1761 (1968).

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Thermochemistry of the Liquid System Lead Oxide–Silica at 900°

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Received August 16, 1968

The partial enthalpies of liquid lead oxide and of solid silica (quartz) in lead–silicate melts have been measured calorimetrically at 900°. The partial enthalpies show a region of sharp dependence on composition near $N_{SiO_2} \simeq 0.35$. This is atrributed to the formation of the orthosilicate anion, $SiO_4{}^{4-}$. The enthalpy data show no evidence for the presence of any other simple silicate anion. The partial enthalpies are compared with available data on the partial excess free energies of mixing. The entropy data similarly are consistent with formation of the orthosilicate anion.

Introduction

In recent years there have been several different thermodynamic investigations of the liquid system $PbO–SiO_2$, based on emf and phase-equilibrium methods. The most recent studies known to the authors are that of Sridhar and Jeffes,[1] who made use of a formation cell

$$Pb(l)\,|\,PbO \text{ or } PbO–SiO_2\,|\,Pt;\ O_2(g)$$

and that of Kozuka and Samis,[2] who used a solid-electrolyte concentration cell of the type

$$Pb(l)\,|\,PbO(l)\,|\,ZrO_2 + CaO\,|\,PbO–SiO_2(l)\,|\,Pb(l)$$

The activities of PbO determined in these two studies do not differ very much. The values reported by Sridhar and Jeffes also agree very well with the earlier results of Richardson and Webb,[3] who measured the activities of PbO in $PbO–SiO_2$ melts on the basis of the oxygen content of liquid lead in equilibrium with lead–silicate mixtures. As a result of these earlier studies it would seem that the activities of PbO, say at 1000°, are known within reasonable limits of error. Since the activities of SiO_2 are related to those of PbO through the Gibbs–Duhem relation, we also have acceptable information on the activities of SiO_2.

In each of the quoted earlier studies, use is made of the temperature dependence of the activity to derive information on the partial enthalpy and entropy of the two components. It should come as no surprise to the critical reader that these derived enthalpy and entropy values differ a great deal from one study to the other (see, *e.g.*, Figures 7 and 8 of ref 1 and Figures 5 and 6 of ref 2). This represents the background for the present investigation, which was aimed at the direct measurement of the partial enthalpies of PbO and SiO_2 in $PbO–SiO_2$ melts at 900°. When our new enthalpy values are compared with the corresponding excess free energies (derived from the cited emf and equilibrium studies), we should obtain a more reliable picture of the behavior of the excess entropies.

The present investigation is an extension of recent work by Holm and Kleppa[4] on the thermochemistry of the liquid system $PbO–B_2O_3$. As these authors did

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[1] R. Sridhar and J. H. E. Jeffes, *Bull. Inst. Mining Met.*, **C76**, 43 (1967).

[2] Z. Kozuka and C. S. Samis, submitted for publication.

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[4] J. L. Holm and O. J. Kleppa, *Inorg. Chem.*, **6**, 645 (1967).