ethanol was added to 1.33 g. (0.0049 mole) of R_2SnCl_2 in about 5 ml. of ethanol. The solution was warmed on a steam bath for a few minutes to coagulate the insoluble NaCl. The solid was filtered off and the solvent removed at 1 mm. with gentle warming (about 40°). The residue was crystallized by dissolving it in hot benzene and slowly evaporating on a rotary evaporator to give 1.0 g. (64%) of $R_2Sn(SCN)_2$, m.p. 184–187° dec.

Anal. Calcd. for $C_8H_{10}N_2S_2Sn$: C, 30.30; H, 3.19; SCN, 36.63. Found: C, 30.57; H, 3.40; SCN,[7] 36.58.

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[7] Determined by Dr. S. M. Nagy by precipitation of silver thiocyanate with silver nitrate in ethanol.

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Raman Spectrum of Solid Perchloric Acid and the Nature of the Solid Phase

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Anhydrous perchloric acid is a well characterized compound in the gaseous and liquid phases. Recently, however, the phase diagram for the system Cl_2O_7–H_2O has been studied[1] and the results of the investigation interpreted as indicating that no compound exists in the solid for a 1:1 ratio of the heptoxide to water. Instead, the equilibrium

$$3HClO_4 \rightleftarrows Cl_2O_7 + H_3OClO_4$$

was postulated to exist at the 1:1 composition with the position of the equilibrium being shifted almost completely to the right at low temperatures. The solid material corresponding to a 1:1 mole ratio of H_2O and Cl_2O_7 was considered to be a mixture of two phases, most likely Cl_2O_7 and H_3OClO_4, although the possibility of a hydrate of Cl_2O_7 also was mentioned.

Recent infrared investigations of solid anhydrous perchloric acid[2] and solid Cl_2O_7[3] do not appear to support this interpretation.

The possibility of such an equilibrium was not considered in the infrared papers, however, and since most of the strong infrared bands of Cl_2O_7 are overlapped by those of perchloric acid, it was felt that a Raman spectrum of the solid might be of interest. A Raman spectrum of crystalline perchloric acid has not been reported previously.

Experimental

Anhydrous perchloric acid was prepared in a vacuum line having no joints or stopcocks using the general procedure of Smith.[4] A calorimetric determination of its melting point[5] gave a value of −102°, which agrees with the Russian value[1] but is appreciably higher than the figure of −112° previously accepted. Details will be published elsewhere. The spectroscopic sample was distilled three times, the last time directly into a small 7-mm. diameter glass tube which served as the cell. After freezing the material in liquid nitrogen, the tube was carefully sealed off to prevent exposure to the atmosphere. Prior to taking the Raman spectrum, the sample was melted three times, the liquid being kept at a temperature just above its melting point to ensure that the equilibrium, if such did exist, would be attained. The spectrum was obtained with the sample tube immersed in liquid nitrogen.

TABLE I

OBSERVED RAMAN BANDS OF SOLID $HClO_4$ (IN CM.$^{-1}$)

Raman		Infrared	
This research	$HClO_4(l)$[8]	$HClO_4(s)$[2]	Assignments
	284		
		346	
		371	Sym. OClOH def.
436 ± 8 w	424	428	Asym. OClOH def.
		478	OH torsion
		566	Sym. OClO def.
585 m	577	585	Asym. OClO def.
		603	
738 s	740	740	
		760	In-phase $HOClO_3$ str.
1038 vs	1031	1033	Out-of-phase $HOClO_3$ str.
	1210 v br	1200	(478 + 760 = 1238)
1243 w		1245	OH def.
		1283	Sym. ClO_3 str.
		1315	Asym. ClO_3 str.
1550 ± 3 vvw			
2329 w			(N_2, gas value = 2330.7)
3040 ± 4 vvw			
3336 ± 5 w	3350 v br	3260	OH str.

The experimental procedure for obtaining the Raman spectrum was similar to that described by Schrader.[6] The sample was illuminated on one side with spectrally pure Hg 4358 radiation and the light scattered from the opposite side, after four reflections from multilayer interference filters to reduce the intensity of the exciting line, was focused on the slit of the spectrograph. The exposure time was 24 hr. using a heat sensitized Eastman IIa-O plate.

The observed frequencies are listed in Table I together with the Raman values for liquid perchloric acid and infrared data for the solid. Uncertainties in the experimental values are about 2 cm.$^{-1}$ except where noted.

Discussion

Inspection of the values given in Table I shows good agreement between the data obtained in the present case and those recorded in the literature for liquid perchloric acid,[7] the principal difference being in the OH bands which were much sharper in the solid.

No indication was obtained of the presence of the very intense 921 cm.$^{-1}$ vibration of H_3OClO_4[8] nor of the 501 and 695 cm.$^{-1}$ vibrations of Cl_2O_7.[9] Interference with any of these bands in the Raman spectrum is unlikely and their absence indicates that

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[1] A. A. Zinov'ev and V. Ya. Rosolovskii, *Zh. Neorgan. Khim.*, **10**, 2383 (1958).

[2] P. A. Giguère and R. Savoie, *Can. J. Chem.*, **40**, 495 (1962).

[3] R. Savoie and P. A. Giguère, *ibid.*, **40**, 991 (1962).

[4] G. F. Smith, *J. Am. Chem. Soc.*, **75**, 184 (1953).

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[6] B. Schrader, F. Nerdel, and G. Kresze, *Z. physik. Chem.* (Frankfurt), **12**, 132 (1957).

[7] A. Simon and M. Weist, *Z. anorg. allgem. Chem.*, **268**, 301 (1952).

[8] R. C. Taylor and G. L. Vidale, *J. Am. Chem. Soc.*, **78**, 5999 (1956).

[9] R. Fonteyne, *Natuurw. Tijdschr.* (Ghent), **20**, 275 (1938).

neither of the two species in question was present in the solid in appreciable amounts.

The assignments in Table I are taken from the paper on the infrared spectrum of the solid.[2] In view of the fact that the crystal structure of solid perchloric acid is not known, there appears to be no point in making a detailed discussion and comparison of the Raman and infrared results. One interesting difference, however, is that the strong Raman band at 740 cm.$^{-1}$ was observed[2] only as a partly resolved shoulder on a more intense infrared band at 760 cm.$^{-1}$. No indication of the latter band was observed in the Raman spectrum. The molecular motion involved presumably corresponds to the breathing frequency of the ClO_4^- ion so that only one fundamental of the molecule is to be expected in this region. It is possible that the overtone of the infrared band at 371 cm.$^{-1}$ is involved and is causing two bands to appear. However, the intensity ratio of the two infrared peaks is reversed from what one would expect if the Raman band is the fundamental and the full explanation is not immediately apparent. The bands in the neighborhood of 550 cm.$^{-1}$ in the infrared spectrum presumably derive from the triply degenerate deformation modes of the ClO_4^- ion. Although individual lines were not resolved in this region of the Raman spectrum, the band listed at 585 cm.$^{-1}$ was rather broad, suggesting the presence of unresolved components.

The failure to detect spectroscopically the presence of either Cl_2O_7 or H_3OClO_4, together with the excellent agreement between the Raman lines of the solid and liquid perchloric acid, serves as excellent evidence that the interpretation of the phase diagram proposed by Zinov'ev and Rosolovskii is in error. In seeking reasons for their apparent misinterpretation, it can be noted that these workers analyzed their samples titrimetrically. In this region of the phase diagram, the composition in terms of mole per cent is quite sensitive to small errors in the weight per cent. This fact, together with the observation that the data points near the 1:1 composition were not numerous, makes it probable that the true nature of the diagram in this region was not delineated. A more detailed investigation appears desirable to clarify the situation.

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On the Properties of Monochlorodiborane

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Preparation of diborane by the hydrogen reduction of boron trichloride proceeds through the formation of chloroboranes.[1-3] Separation of these reactive intermediates from synthesis mixtures, however, is extremely difficult by conventional vacuum-line fractionation. As a result, the successful isolation of chloroboranes has been reported only twice,[4,5] and little knowledge exists relative to properties of the pure compounds.

By using low temperature gas chromatography techniques, we recently have resolved two major intermediates in the diborane synthesis, $BHCl_2$ and B_2H_5Cl.[6] In the present investigation, preparative gas chromatography methods were employed to obtain sufficient quantities of monochlorodiborane for physical measurements and chemical reactivity studies. Contrary to all previous indications, we have found the pure compound to be comparatively stable. No detectable decomposition occurred at 25° in a 1-hr. period for samples maintained at pressures less than 300 mm. Samples stored at 0° were unchanged after 8 hr.

With quantities of purified B_2H_5Cl available, it has been possible to establish the sequence in dichloroborane disproportionation at 30° to proceed from $BHCl_2$ through B_2H_5Cl to B_2H_6. The initial step

$$5BHCl_2 \longrightarrow B_2H_5Cl + 3BCl_3$$

has not been reported previously. This reaction is easily reversible and can be made to go completely to the left when a large excess of liquid BCl_3 is present. Although no unidentified peaks appeared in the gas chromatograms or infrared spectra, it is unlikely that the reaction could proceed without the formation of other, short-lived, intermediates.

During disproportionation of B_2H_5Cl (to B_2H_6 and BCl_3) at 35° under 1 atm. of nitrogen, the secondary reaction of BCl_3 with unreacted B_2H_5Cl leads to the presence of $BHCl_2$ in the final mixture. The reaction is extremely slow, reaching equilibrium only after 70 hr. In the presence of finely divided B_2O_3, however, the rate of B_2H_5Cl disproportionation is greatly increased. The products of this reaction are B_2H_6 and a substance sorbed on the B_2O_3 [probably of the general formula $(BOCl)_x$][7] that gives off BCl_3 when heated under vacuum.

Monochlorodiborane reacts rapidly with HCl in the vapor phase at 25°. With a relatively large mole ratio of HCl/B_2H_5Cl, the reaction is quantitative

$$B_2H_5Cl + 5HCl \longrightarrow 2BCl_3 + 5H_2$$

When HCl was added to B_2H_5Cl in small increments, conversion to $BHCl_2$ was observed to be an intermediate step in the reaction.

Vapor pressure measurements of B_2H_5Cl are recorded in Table I. The calculated values were obtained from

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