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Infrared Spectra of the Vapors Above Rhenium Heptoxide and Sodium, Potassium, Rubidium, and Cesium Perrhenates: Tetrahedrally Coordinated Rhenium Compounds[1b]

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Received April 2, 1968

Infrared spectra (4000 to 400 cm^{-1}*) were measured for the vapors above rhenium heptoxide,* Re_2O_7 *(180 to 250°C), and Na, K, Rb, and Cs perrhenates,* $MReO_4$ *(800 to 1100°C). Bands for the heptoxide coincide closely with those for* ReO_3Cl *and* ReO_3Br *and are consistent with a pseudohalide structure* $O_3Re{-}O{-}ReO_3$*. The Re–O–Re stretching modes are assigned to bands at 870 and 690 cm*$^{-1}$*. The Re–Cl stretch of* ReO_3Cl *is reassigned to a band at 434 cm*$^{-1}$*. For all the alkali perrhenates, only one broad band is observed at 900 cm*$^{-1}$ *and probably is due to both monomer and dimer. This spectrum is close to that of the* ReO_4^- *group. The frequencies of gaseous perrhenic acid,* $HOReO_3$*, are discussed.*

Introduction

Previous papers[2] have dealt with systematics in the infrared spectra of gaseous, tetrahedral oxohalides and related molecules containing central atoms from Groups V and VI. The present study deals with molecules containing the Group VII element Re. These spectra afford the opportunity to examine whether structural conclusions concerning oxohalides can be extended to other types of compounds including binary and ternary gaseous oxides.

Gaseous Re_2O_7 [3.6] is believed to have local C_{3v} geometry around the rhenium atoms, with three double bonded oxygens and one single bonded bridging oxygen. As such, the structure should be similar to that proposed for gaseous perrhenic acid[5] and to those known for the oxohalides, ReO_3X ($X=F$, Cl, Br).[7,8] The infrared spectrum of the heptoxide is thus expected to give both structural evidence, and possibly the frequency of a Re–O single bond stretching mode.

Potassium perrhenate sublimes without decomposition[9,10] and consequently offers the possibility to study the spectrum of a gaseous, ternary oxide. From electron diffraction data[11] for the vapors above $KReO_4$, a C_{3v} structure, $KO{-}ReO_3$, was deduced. Recent work[12] by Drowart and his collaborators on $NaReO_4$ and $KReO_4$ indicates that the vapor is composed of both monomer and dimer and leaves the electron diffraction work[11] open to serious doubt. In a related study, Büchler *et. al.*, have found that the gaseous cesium[13] and lithium[14] sulfates have no dipole moment, indicating that each alkali atom is symmetrically located with respect to two of the oxygens, and perhaps that the gaseous species is best described by a structure $(Cs)_2(SO_4)$ with D_{2d} symmetry. Again, this is in contrast to electron diffraction work[15] which was interpreted in terms of a $(Cs{-}O{-})_2SO_2$ structure analogous to those of the sulfonyl halides or sulfuric acid.[16]

To help answer these questions about the structure of the gaseous binary oxide, Re_2O_7, and of the gaseous ternary oxides $MReO_4$ ($M=Na$, K, Rb, Cs), an infrared spectral study of the vapors above the respective compounds was undertaken.

Experimental Section

Potassium perrhenate and rhenium heptoxide were products of Alfa Inorganics Co., Beverly, Mass. The sodium, rubidium, and cesium salts were synthesized[17] from the oxide and the alkali carbonates and were recrystallized from water.

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(1) (a) An Advanced Research Projects Agency Interdisciplinary Laboratory. (b) Supported by the United States Army Research Office-Durham. The infrared spectrometer was acquired in part from a National Science Foundation Institutional Facilities grant. (c) On leave from the Istituto di Chimica Fisica ed Elettrochimica, Università degli Studi di Roma, Rome, Italy.

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Either mullite ($2\,Al_2O_3.SiO_2$) or stainless steel sample tubes and nickel or alumina boats were used with the appropriate vacuum and window connections. Other details have been given previously.[16] Superheating experiments were carried out in the mullite cells as follows: the sample was placed in a narrow mullite tube with one end closed. The open end was placed in the center of the hot zone of the cell; the closed end with sample was in the cold zone and heated in some cases with a separate Kanthal (Kanthal Corp., Stamford, Conn.) winding. In addition to the usual[16] Kanthal furnace with 45 cm hot zone, a molybdenum wound furnace[18] with 15 cm hot zone, and capable of 1800° was used. Temperature was measured with Chromel/Alumel or Pt/Pt–10% Rh thermocouples. Argon and oxygen at one atm were used for the gas diffusion barrier and to prevent decomposition.

Temperature was recycled during the runs as a means of distinguishing between spectra due to the desired molecule(s), decomposition products, and window bands. Emission spectra were taken using the internal chopper of the Beckman IR-9 grating spectrometer (4000-400 cm^{-1}).

Results and Discussion

Rhenium Heptoxide, Re_2O_7. Bands were first observed at ~180° and were strongly saturated at 250°C. Frequencies and assignments are presented in Table I, together with those of ReO_3Cl, ReO_3Br,[8] and $Cr_2O_7^{2-}$. The Re_2O_7 frequencies correspond closely with those of the perrhenyl halides, including overtones and combinations. The main exceptions are the broad bands at 690 and 870 cm^{-1} observed for the heptoxide. The spectrum is explained by assuming that the heptoxide has the structure $O_3Re–O–ReO_3$ with local C_{3v} symmetry around each Re. The coupling between the ReO_3 vibration modes is expected to be small so that the in and out-of phase motions are nearly degenerate.[19]

The bands at 690 and 870 cm^{-1} are attributed to the symmetric and antisymmetric Re–O–Re strentching motions. For the S–O(H) and the S–F gas phase stretching vibration modes, the respective frequencies are approximately in the ratio (1.1): 1.[2] The Re–F frequency has not been measured, but the following estimations can be reasonably made. For the gaseous, monomeric oxohalides of V,[20,21] Cr,[20] Nb,[22] Mo,[23,24,25] W,[25] and Re[8] the metal-oxygen «double bond» stretching frequencies are sensibly constant at 1000 cm^{-1} as they are, in fact for other transition elements.[26] For all except Re, the assigned metal-chlorine[20-25] stretching frequencies are at about 450 cm^{-1}. It seems likely therefore that the ReO_3Cl band at 434 cm^{-1} be reassigned to $\nu_3(a_1)$, the Re–Cl stretch. Metal-fluorine stretches are known for V,[21] Cr,[20] and Mo[25] and lie near 700 cm^{-1}. By assuming that the ratio ν(M–F)/ν(M–Cl) is constant for all these elements and by taking ν(Re–Cl) as 434 cm^{-1}, ν(Re–F) is calculated to be 690 cm^{-1}. The Re–O–Re stretching frequencies

Table I. Infrared Absorption Frequencies (cm^{-1}) of Some ReO_3X (X=Cl, Br, $OReO_3$) Molecules

ReO_3Cl [a] Liquid	ReO_3Br [a] Liq., Solution	Re_2O_7 Vapor	Approx. Description [b]	$Cr_2O_7^{2-}$ [c]
196 m [d]	168 m		$\nu_6(e)$	
293 s	195 m		$\nu_3(a_1)$, Re–X [e]	
344 s	332 s		$\nu_5(e)$, ReO_3 def.	
	342 m		$2\nu_6$	
434 vs	350 m		See below [e]	
	581 vw		$3\nu_3$	
		690 w, b	ν_s(Re–O–Re) [f]	560
776 vw			344+434	
		870 s, b	ν_{as}(Re–O–Re)	780
921 vw, sh		920 w		
		965 sh		
960 vvs	963 vs	976 } s	$\nu_4(e)$, Re–O_3 str.	~945
		986 sh		
1001 vs	997 s	1000 w, sh	$\nu_1(a_1)$, Re–O_3 str.	~895
		1050 vvw		
1156 w	1136 w		$\nu_6+\nu_4$	
1304 vw		1298 vw	$\nu_5+\nu_4$	
1926 w	1929 w	1950 vvw	$2\nu_4$	
1961 m	1963 m	1977 vw	$\nu_4+\nu_1$	
2002 vvw	1993 vvw		$2\nu_1$	

[a] Miller and Carlson.[8] [b] The notation used in this table for the description of Re_2O_7 vibrations is arbitrarily that for ReO_3X, C_{3v}. [c] H. Stammreich, D. Bassi, O. Sala, and H. Siebert, *Spectrochim. Acta, 13,* 192 (1958). [d] b=broad, s=strong. m=medium, w=weak, sh=shoulder, str=stretch, v=very. [e] Miller and Carlson assigned these bands $\nu_2(a_1)$, ReO_3 deformation. It now seems more likely that $\nu_3(a_1)$, Re–Cl stretch, be at 434 cm^{-1} (see text). This implies that the Re–Br stretch be at 330-350 cm^{-1}. Work on the fluoride is desirable. [f] This band could also be assigned to $2\nu_5$. See text.

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should consequently have an average value 10% higher or 760 cm^{-1}. On this basis, and because of their broadness, the bands at 690 and 870 cm^{-1} are both assigned to the Re–O–Re stretches; the possible assignment of the former to 2ν_5 is precluded. This assignment agrees well with that for the isoelectronic $Cr_2O_7^{2-}$.

This pseudohalide structure is similar to that deduced for Cl_2O_7.[27] These results add support also to the hypothesis[28] that the oxohalides are model compounds for the prediction of frequencies of such high molecular weight oxides as V_4O_{10} and $(WO_3)_3$.

The Perrhenates of Na, K, Rb, and Cs. All spectra were observed at nominal temperatures of 800° to 1100°C. Band frequencies were, within experimental error, independent of which alkali atom was involved. Only the features shown in Figure 1 were observed.

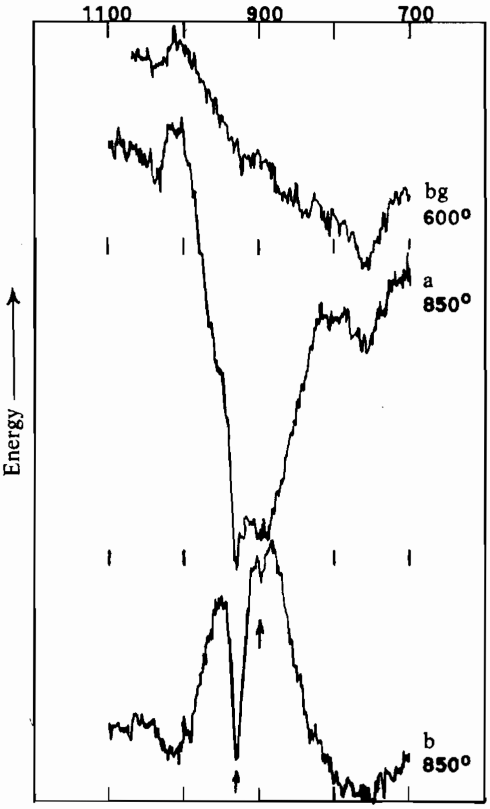

Figure 1. Spectrum of the vapors above $KReO_4$ between 1100 and 700 cm^{-1}: Energy *vs* frequency in cm^{-1}; bg, background spectrum at 600°C; (a) absorption at 850°C; (b) emission at 850°C. The spectra were taken using a mullite sample tube in a furnace with 45 cm long hot zone. The features at 900 and 930 cm^{-1} (marked with arrows) were more prominent in absorption spectra measured using a 15 cm hot zone furnace and are assigned to condensed species.

In absorption (Figure 1a) these include (arrows) a sharp, intense peak at 930 cm^{-1} and a much weaker sharp peak at 900 cm^{-1}. (The latter is seen more clearly in spectra taken using the 15 cm long furnace). Both of these overlap a broad peak extending from 800 to 1000 cm^{-1} and centered at 900 cm^{-1}. The broad feature is clearly evident in emission (Figure 1b) but the two sharp features at 900 and 930 cm^{-1} are seen only in absorption. They are relatively stronger in a furnace with a shorter hot zone. The broad feature is thus due to species in the hot zone; the sharp bands are due to condensable species in a cooler region of the furnace.

On the basis of these observations and similar observations by Büchler and Marram[29] on the metaborate system, the two sharp bands are assigned to a condensed perrhenate and the broad one to the gaseous monomer and/or dimer. The two sharp bands have the same frequencies and shapes as those observed for potassium and ammonium perrhenates in KBr disc spectra.[30]

Even with the superheating conditions normally used, a monomer to dimer ratio of at least 1:2 was expected. Extensive superheating, did not cause any change in frequencies or in band contours. Consequently, the broad band must in part be assigned to the monomer; the dimer band is possibly not much shifted[31] and is taken to coincide with the monomer band.

In addition to the above gas phase bands, a sharp window (thin film) band was observed at 908 cm^{-1} for all four perrhenates and coincides with a band in the KCl disc spectrum of Re_2O_7.[32]

Table II. Summary of Re—O Vibration Frequencies Observed for ReO_3X, ReO_4^-, and Re—O—Re

		Frequencies	Weighted Average
ReO_3X	vapor, liquid	1000 (a_1)	980
	X=Cl, Br,[b] $OReO_3$[c]	970 (e)	
ReO_4^-	water,[d] DMF,[c] thin film,[c]	915 (f_2)	929
	KBr Disc,[e] Nujol.[f]	971 (a_1)	
	Water, Raman.[d]		
Re—O—Re	Vapor[c]	870	780
		690	

[a] Weighted according to statistical weight of symmetry species shown. [b] Miller and Carlson.[8] [c] This work, dimethylformamid. [d] Claassen and Zielen.[33b] [e] Sadtler Laboratories.[30] [f] Busey and Keller.[33c]

Available data for Re—O vibrational modes frequencies are summarized in Table II. For each type of compound indicated there is very little scatter; *e.g.*, for ReO_4^- [33] the f_2 vibration frequencies in the various environments listed fall within 15 cm^{-1} of 915. The gas phase perrhenate frequency presently observed, 900 cm^{-1}, falls very close to this condensed phase ionic frequency. If the structure were O_3Re—O—K, analogous to that of the perrhenyl halides,

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bands would have been expected at 1000, 970, and 780 cm^{-1}. This is not the case. For the gaseous alkali perrhenate monomer, the vibration frequencies (and probably the band distances) seem to be best approximated by values for the ReO_4^- ion.

Gaseous $HReO_4$ is, by analogy with the sulfuric acid system,[2,16] best approximated by slight modification of the ReO_3F frequencies, as indicated also in the discussion of the Re–O–Re frequency.

Conclusion

The spectrum of gaseous rhenium heptoxide corroborates a pseudohalide structure with bridging oxygen bonds: $O_3Re–O–ReO_3$. The only other transition element system of this type to be studied is $(MoO_3)_n$ [24] where the pseudohalide model also explains the infrared spectrum.

The spectra of the four gaseous perrhenates are identical to one another and similar to those for the ReO_4^- group, in agreement with previous infrared spectral results for metaborates[29,34] and with the electric deflection studies for sulfates.[13,14]

Acknowledgments. Professor Alan W. Searcy pointed out the interesting volatility of the perrhenates to F. E. Stafford in 1959. The help and discussions of Dr. Brian G. Ward of this laboratory is much appreciated. Dr. Alfred Büchler, Professor Jean Drowart, and Professor Davide White provided us with unpublished data. Mr. Jim Hahn and Mr. Fred Riske provided technical assistance.

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