four acids, it is reasonable that it was not possible to observe any association for H_2SO_4 in the vapor state at the higher temperature used.

Attention is called to Table VI in ref 8 as corrected here for $ClSO_3H$, where shifts in the stretching frequencies of sulfuric and sulfonic acids with the change of phase from liquid to the monomolecular state are compared. The present study confirms the conclusion arrived at in that paper and explains the discrepancies noted there.

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Infrared Spectra of Some Gaseous Molybdenum Oxides and Oxyhalides

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Abstract: A special high-temperature, gas-diffusion barrier cell has been used to examine the spectra from 4000 to 400 cm^{-1} of some involatile molybdenum compounds. For MoO_2Cl_2 the symmetric and asymmetric Mo=O stretches are at 972 and 990 cm^{-1}, and for MoO_2Br_2 at 969 and 991/999 cm^{-1}. An Mo–Cl stretch was observed at 450 cm^{-1}. For the vapors above MoO_3(s), bands were observed at 969 and 815 cm^{-1}. For $MoOCl_4$, a band at 1015 cm^{-1} is assigned to the Mo=O stretch. Predictions are made for H_2MoO_4 and H_2CrO_4. Heating MoO_3(s) plus HCl gives rise to the MoO_2Cl_2(g) bands.

The existence of several gaseous molybdenum oxides and oxyhalides, including $(MoO_3)_n$, MoO_2Cl_2, MoO_2Br_2, $MoOCl_4$, and $MoO(OH)_2Cl_2$ has been reported.[1] There has been some spectrometric work on the solid compounds, but none to our knowledge on the vapor phase infrared spectra. The latter would be of particular interest in evaluating the systematics of the structure and the thermodynamic properties of various high-temperature systems.

Berkowitz, Inghram, and Chupka[2] report a mass spectrometric investigation of the vapors from MoO_3 in a molybdenum Knudsen cell at 525° and found that the most abundant species was Mo_3O_9, with lesser amounts of Mo_4O_{12} and Mo_5O_{15} and only a slight trace of MoO_3 and Mo_2O_6. Owing to the surprising stability of the polymeric species at high temperature, they postulated a puckered, hexagonal ring structure. The same structure is reported for the similar trioxane vapor,[3] and for the analogous $(SO_3)_3$[4,5] and $(SeO_3)_n$.[6]

The formation of solid MoO_2Cl_2 by direct reaction of MoO_2 with Cl_2 has been reported.[7,8] Sutton reports[9] early electron diffraction work indicating that MoO_2Cl_2(g) has a tetrahedral configuration.

The increased volatility of molybdenum and its oxides in the presence of water vapor at high temperature has been reported[10-12] and is explained by the formation of H_2MoO_4. It is likely that this molecule is analogous to H_2SO_4 and fits into a series MoO_2X_2 with X = F, OH, Cl, Br.

$MoOCl_4$ has been prepared[13,14] in various ways, including a high-yield method[14] involving direct oxidation of $MoCl_5$ at 215°. The analogous SOF_4(g) is well characterized spectroscopically and structurally.[15-17] On the other hand, there seems to be a great deal of ambiguity concerning the presumably analogous gaseous $MoO(OH)_2Cl_2$.[7,8,18,19] Reaction of

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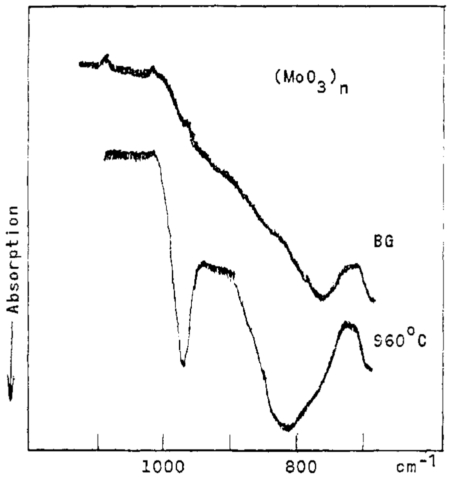

Figure 1. Spectrum of the vapors above MoO_3 solid at a nominal temperature of 960°. The peaks are at 969 and 815 cm^{-1}.

HCl with MoO_3 reportedly forms the solid compound and is often used to purify the trioxide by vapor-phase mass transport. Hultgren and Brewer[20] report a high-temperature law of mass action study that indicates that MoO_2Cl_2 and H_2O are the principal vapor phase species.

In other papers[21,22] of this series, the systematics of the spectra of gaseous X–SO_2–Y, and X_2YPO, where X or Y is F, OH, Cl, etc., have been examined, particularly as regards variation of the X and Y. The purpose of the present paper is to see to what extent the same systematics may apply to the structurally related X–MoO_2–X and $MoOX_n$.

Experimental Section

A modified Beckman IR-9 spectrometer was used as described previously[21] for obtaining the spectra in the region 400–4000 cm^{-1}. The sample was contained in a 1-m tube, the central 18 in. of which were heated by a Kanthal[23] wound tube furnace. The central 24 in. of the tube were made of mullite. Each end fused to the mullite was made from Pyrex glass with fittings so that a AgCl window could be held in place using O rings and a brass collar. One of the glass ends of the tube had a side arm for evacuation and admission of gases. To eliminate the effects of background radiation due to the heated tube and gases, the light from the external Nernst Glower was chopped at 11 cps before it entered the tube. Temperature measurement was made by means of a chromel–alumel thermocouple located between the tube and the tube furnace. The spectra were all taken in a 1 atm argon atmosphere except when HCl gas or O_2 gas were used as reactants. Then 0.5 atm of each gas was used and the total pressure monitored during the run.

The usual tests of temperature dependence of band intensity during repeated cycling and dependence on the pressure of reactant gases or evacuation were used to assign the bands to the gaseous, high-temperature species. In addition, substances were identified by the characteristic color of the vapors and of the crystals which would form in the cooler portions of the tube. All samples were used as received. Possible impurities in the MoO_2 or MoO_3 were removed by heating *in situ* to 500° and holding under vacuum for several hours.

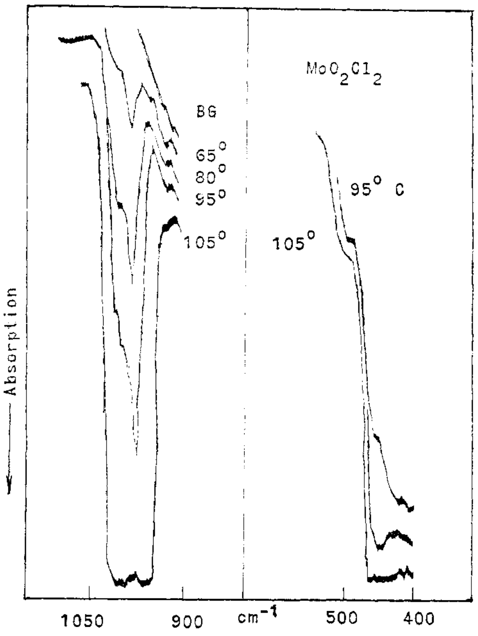

Figure 2. Spectrum of gaseous MoO_2Cl_2. The peaks and shoulders observed at a nominal temperature of 95° are at 994, 984, 972, and 450 cm^{-1}.

Data and Results

Molybdenum Trioxide. A spectrum due to the vapor over solid MoO_3 (99%) was observed at a nominal temperature of 950°. There were peaks at 969, 815, 2390, and 3720 cm^{-1}. Only the first two peaks disappeared on cooling. The other two peaks correspond to CO_2 peaks and probably came from a carbonate impurity. On cooling the sample to 700° and holding it under vacuum for several hours the impurity was removed. When the sample was again heated to 950°, only the 969- and 815-cm^{-1} peaks appeared. These peaks disappeared on cooling and are shown in Figure 1.

A sample of molybdic acid (85%) was heated under vacuum to 300°. Then argon was admitted and the spectrum scanned as the temperature was increased. At 950° peaks corresponding to those of MoO_3 were seen, but there were no peaks in the OH bending or stretching regions to indicate the presence of any hydroxides.

Molybdenum Dioxodichloride. This compound was prepared *in situ* by the reaction[7,8,14]

$$MoO_2(s) + Cl_2(g) = MoO_2Cl_2(g)$$

Spectra of the vapor above MoO_2 (City Chemical Corp., New York, N. Y., 99.8%) were observed between 25 and 900°. There was no observed change from the background as was expected since MoO_2 is involatile at these temperatures. The MoO_2 was placed in the tube furnace and baked under vacuum at 500° for several hours to remove any volatile impurities. After cooling, 0.5 atm each of chlorine and argon gas were added and the system was slowly heated as the spectra were scanned. At room temperature there was a band at 2600–3100 cm^{-1} indicating the presence of HCl due to an impurity in the Cl_2 gas. At about 65° an absorption band appeared at 972 cm^{-1}. At 95° this band was very pronounced and at 105° the band showed total absorption. There was also a band at ~450 cm^{-1} which is a region of poor performance of the instrument. At this temperature, yellow crystals began condensing onto the cooler portions of the tube. The furnace was cooled and the 972- and 450-cm^{-1} bands disappeared. The furnace was reheated and these two bands reappeared. There were also very weak peaks at 1960 and 1830 cm^{-1}. On cooling, all of the peaks disappeared at the same rate and were therefore due to the same compound. With a resolution of 1 cm^{-1}, the peak at 972 cm^{-1} was seen to have shoulders at 984 and 994 cm^{-1} as shown in Figure 2.

In work done previously by Mr. Gerald Estes, the preparation of MoO_2Cl_2 was attempted by reacting MoO_3 and chlorine gas. Several absorptions were observed including ones seen here. The others were probably due to impurities.

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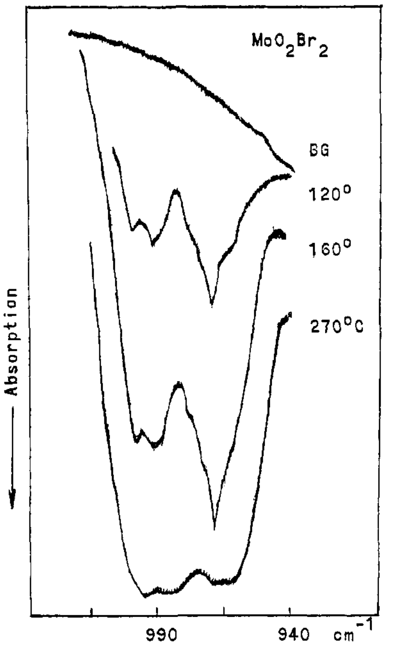

Figure 3. Spectrum of MoO_2Br_2. The peaks are at 999, 991, and 969 cm^{-1}.

Molybdenum Dioxodibromide. This compound was prepared by adding a few drops of liquid bromine to the previously baked MoO_2 and heating *in situ*. At about 120° peaks appeared at 969 and 995 cm^{-1}. There was also a peak at 1360 cm^{-1}. The tube was heated to 270° where total absorption occurred at the peak frequency and orange crystals condensed onto the cooler portions of the tube. On cooling, all peaks except that at 1360 cm^{-1} disappeared. The furnace was reheated to 160° where the spectrum was observed at a resolution of 1 cm^{-1}. The observed maxima are at 969, 991, and 999 cm^{-1}, as shown in Figure 3.

The sample was cooled and the peaks disappeared. Then Cl_2 gas was added and the sample reheated. The MoO_2Cl_2 band at 972 cm^{-1} and the band at 450 cm^{-1} reappeared at about 95°. There were also the very weak peaks at 1960 and 1830 cm^{-1}. There was no detectable mixed halide or bromide spectrum.

Molybdenum Dioxodiiodide. It was attempted to prepare this compound by passing iodine vapor over hot MoO_2, but no reaction was observed up to 600°. This is expected by analogy with chromium and sulfur.

Molybdenum Oxodihydroxydichloride. It was attempted to prepare this coumpound by the reaction of HCl gas (Matheson, 99.9%) with MoO_3. At 85° a peak appeared at 972 cm^{-1}. With heating up to 105°, this developed into a peak identical with that of MoO_2Cl_2 shown in Figure 2, but there was also a peak at 1740 cm^{-1} in addition to the MoO_2Cl_2 peak at 450 cm^{-1}. There was no apparent change in the H_2O peak intensities.

Molybdenum Oxotetrachloride. It was attempted to prepare this compound *in situ* using the method of Mallock.[14] The reaction is

$$MoCl_5 + {}^1/_2O_2 = MoOCl_4 + {}^1/_2Cl_2$$

The reactants were heated with an argon atmosphere. As the temperature was increased, peaks appeared at 1015, 970, and 450 cm^{-1}. It was decided that some of these peaks were due to impurities. A sample of $MoOCl_4$ was prepared and distilled in a vacuum line, sealed into an ampoule, and then broken inside the tube furnace while passing dry nitrogen through the tube. The sample was in the form of green crystals, identical in appearance with those sent to us by Mallock. They melted at about 100° to give a brown liquid which produced a brown vapor at about 120° in agreement with observations in the literature.[13,14] At about 95° a doublet appeared at 1006 and 1017 cm^{-1}. As the temperature was increased, this gradually became stronger until a band at 1015 was formed with only a small shoulder at 1006 cm^{-1}. These peaks are shown in Figure 4.

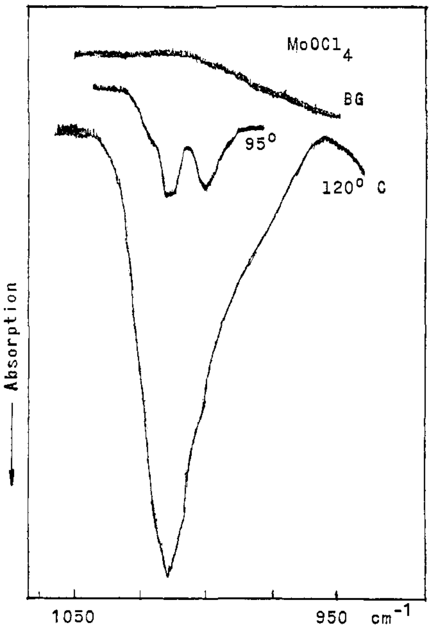

Figure 4. Spectra observed during reaction of $MoCl_5$ with O_2 At 95° the peaks are at 1017 and 1006 cm^{-1}. At 320°, the peak is at 1015 cm^{-1} with a shoulder at 1006 cm^{-1}. This peak is attributed to $MoOCl_4$.

Discussion

The molybdate ion has vibrational frequencies[24] at 936, 895, 365, and 220 cm^{-1} and in general the Mo=O stretching band is in the region 900–1050 cm^{-1}. It would be expected that for MoO_2Cl_2 at least two of the nine fundamental frequencies would be in this region. It would be expected also that many of the frequencies would be lower than the 400-cm^{-1} limit of this instrument. The spectra of MoO_2Br_2 and MoO_2Cl_2 can be interpreted by analogy with the spectra of CrO_2F_2, CrO_2Cl_2, SO_2F_2, and SO_2Cl_2.[24,25] These molecules all have C_{2v} symmetry. For CrO_2Cl_2 the symmetric and asymmetric Cr–O stretches are 990 and 1000 cm^{-1}, respectively. The symmetric and asymmetric Cr–Cl stretches are 475 and 499 cm^{-1}, respectively. All other modes are of lower frequency. For CrO_2F_2 the corresponding frequencies are 1006, 1016, 727, and 789 cm^{-1}. For SO_2F_2 they are 1269, 1502, 848, and 885 cm^{-1}. For SO_2Cl_2 the frequencies are 1182, 1414, 405, and 362 cm^{-1}. Thus it seems probable that the Mo–O symmetric and asymmetric stretches would be fairly close to one another and in the region 900–1050 cm^{-1}. The Mo–Cl stretches should be in the region of 400–500 cm^{-1}. In contrast to the sulfonyl halides, little change would be expected for the Mo–O stretches in exchanging halides although the Mo–X frequencies would change. Thus for MoO_2Cl_2 we assign the 972-cm^{-1} peak to the symmetric Mo–O stretch, and the 984–994-cm^{-1} peaks to the asymmetric stretch. The 450-cm^{-1} peak is assigned to the symmetric Mo–Cl stretch although instrument performance in this region is poor and this peak could be split or have fine structure. For MoO_2Br_2 the 969- and 991/999-cm^{-1} peaks are assigned to the symmetric and asymmetric Mo=O stretches, respectively.

The spectrum of the vapors above MoO_3 is interpreted assuming that only trimer, analogous to $(WO_3)_3$[26]

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[24] K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963.

[25] D. R. Lide, D. E. Mann, and J. J. Comeford, *Spectrochim. Acta*, **21**, 497 (1965).

[26] W. W. Weltner, Jr., and D. McLeod, Jr., *J. Mol. Spectry.*, **17**, 276 (1965).

or $(SO_3)_3$,[4,5] is present. Such an assumption should not be serious where only the Mo=O stretches are concerned. Furthermore, the MO_2 units should be similar to those in the molybdenyl halides. Major bands for the sulfur trioxide trimer are 856, 1228, and 1510 cm^{-1}. These are assigned to a ring vibration and the out-of-phase symmetric and asymmetric S=O stretches. Less intense bands are seen also for the in-phase stretches. If the coupling between the MoO_2 groups is weak, then the in-phase and out-of-phase vibrations would be nearly degenerate.[27] Since in the MoO_2X_2 spectra the symmetric and asymmetric stretches are nearly degenerate at ~980 cm^{-1}, irrespective of whether X is Cl or Br, it is assumed that the four Mo=O stretches are all degenerate at 969 cm^{-1}. The band at 815 cm^{-1} is then assigned to a ring vibration. Matrix isolation work would be desirable to attempt to resolve the bands.

For the vapors above $MoOCl_4$, the band at 1015 cm^{-1} is assigned to the MoO stretch of the gaseous oxotetrachloride. This frequency is somewhat higher than that in the condensed phase[14] and in molybdenyl chloride. For SOF_4[15–17] the stretch lies at 1379 cm^{-1}, almost exactly at the mean of the SO_2F_2 symmetric (1269 cm^{-1}) and asymmetric (1502 cm^{-1}) stretching frequencies.

The shape and the location of the band observed during the reaction of HCl with MoO_3 indicates that MoO_2Cl_2 was present. The origin of the 1740-cm^{-1} band is unexplained. No bands attributable to OH stretching or bending vibrations were observed to indicate the presence of $MoO(OH)_2Cl_2$, nor a shift in the Mo=O band. There was also no observable increase in the water vapor spectrum, but this is very probably due to a combination of background and formation of hydrates in the cool parts of the tube. Thus the present results are in qualitative agreement with those of Hultgren and Brewer.[20]

Conclusion

These results show that the various gaseous molybdenum oxyhalides may be studied readily in the infrared, and also that they should be easily accessible to modern electron diffraction or microwave techniques. To the extent that data are available, there are some differences between the molybdenum and sulfur series. The nature of X in MoO_2X_2 has much less effect on the oxygen frequencies, as is the case for CrO_2X_2, and for X_3VO *vis-à-vis* X_3PO.[2,4,28] In going from SO_2F_2 to SOF_4 neither the average oxygen frequency nor the SO bond length is much changed;[15–17] for the molybdenum oxychlorides, as expected from the ready availability of the d orbitals, there is about a 35-cm^{-1} increase in frequency implying a corresponding decrease in bond length.

By analogy with the chromyl compounds, the molybdenyl fluoride M–F stretches are expected to be centered at ~740 cm^{-1}. As is the case in the X–SO_2–Y and the X_2YPO series,[21,22] the OH should act like a halogen insofar as the spectra are concerned. The Mo=O stretches in H_2MoO_4[10–12] are therefore expected to lie at ~980 cm^{-1}. The M–$(OH)_2$ stretches are similarly estimated to be centered at 830 and 800 cm^{-1}, respectively, for the gaseous chromic and molybdic acid molecules.

Corrleations between the M–O (M = S or Mo) stretching frequencies and bond length or bond order have been suggested by Gillespie and Robinson[29] and by Cotton and Wing.[30] Treating the MoO_2 and the $M[O(H)]_2$ groups as pseudo-diatomics,[29] one obtains force constants of 7.6 to 8.3 and 5.2, respectively, from the measured and the estimated frequencies. For the terminal oxygens, the curves of ref 30, which in fact are for molecules of another geometry, give a Mo–O bond distance of ~1.7 A; for the hydroxyl, ~1.8 A. The corresponding bond orders,[30] on a scale ranging from 0 to 3, are 2.7 for the terminal and 1.9 for the hydroxyl oxygens. For the sulfur compounds, on a scale[29] ranging from 0 to 2, the corresponding bond orders are ~2 and 1.3, respectively. A possible explanation for the high bond order of the metal–hydroxyl oxygen bond is the conclusion[31] that the d orbitals participate in the S–X bonding of X–SO_2–Y.

Acknowledgments. Climax Molybdenum Corporation and, in particular, Dr. A. K. Mallock very generously supplied us with authentic samples of pure molybdenyl chloride and molybdenum oxotetrachloride, as well as with unpublished synthesis procedures. Mr. Gerald M. Estes, National Science Foundation (NSF) Research Participant, performed some of the experimental work and Dr. Scaria Chackalackal provided helpful discussions. T. V. Iorns was an NSF Research Participant. The spectrometer was acquired in part through an NSF facilities grant and the external source electronics carried out by Robert J. Loyd. The work was supported in part by the Materials Research Center and primarily by the U. S. Army Research Office, Durham. In this and in our other work[21,22] we have greatly benefited from the experience of Dr. Alfred Büchler and appreciate his having gvien us a copy of his thesis, Harvard University, 1960.

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(27) H. Gerding and W. J. Nijveld, *Rec. Trav. Chim.*, **59**, 1209 (1940).

(28) See, *e.g.*, H. Selig and H. H. Claassen, *J. Chem. Phys.*, **44**, 1404 (1966).

(29) R. J. Gillespie and E. A. Robinson, *Can. J. Chem.*, **41**, 2074 (1963).

(30) F. A. Cotton and R. M. Wing, *Inorg. Chem.*, **4**, 867 (1965).

(31) M. Spoliti, S. M. Chackalackal, and F. E. Stafford, to be submitted for publication.