Yields (based on carbonyl): 3.9 g. of $Mo(NO)_2Cl_2$, 91%; 4.3 g. of $W(NO)_2Cl_2$, 96%.

$Mo(NO)_2Cl_2(P(C_6H_5)_3)_2$.—$Mo(NO)_2Cl_2$ (1.15 g., 0.005 mole) and triphenylphosphine (3.95 g., 0.015 mole) in benzene were heated under nitrogen for 15 min. at refluxing temperature. The dark green $Mo(NO)_2Cl_2$ completely dissolved to give a clear green solution. The solvent was partially removed under vacuum, pentane added, and the solution cooled. On standing for 30 min., small yellow-green crystals separated. The product was separated by filtration, washed with pentane, and dried under vacuum. The compound was recrystallized from benzene–pentane (2:1); yield 2.1 g., 70%.

$Mo(NO)_2Cl_2((C_6H_5)_3As)_2$, $W(NO)_2Cl_2((C_6H_5)_3P)_2$, and $W(NO_2)$-$Cl_2((C_6H_5)_3As)_2$.—These complexes were obtained following essentially the same procedure as that used for $Mo(NO)_2Cl_2(P(C_6H_5)_3)_2$.

$Mo(NO)_2Cl_2(p\text{-}CH_3C_6H_4NH_2)_2$ and $W(NO)_2Cl_2(p\text{-}CH_3C_6H_4NH_2)_2$.—*p*-Toluidine (1.07 g., 0.010 mole) in acetone (15 ml.) was added, under nitrogen, to a solution of $Mo(NO)_2Cl_2$ (1.15 g., 0.005 mole) or $W(NO)_2Cl_2$ (1.60 g., 0.005 mole) in the same solvent (25 ml.). After a few minutes, the solution became yellow-green in color. The solvent was then removed under vacuum. The residual golden yellow solid was washed with pentane and dried under vacuum. The compound decomposes rapidly in solution and was not recrystallized. Yields: 2.10 g. of $Mo(NO)_2Cl_2(C_7H_9N)_2$, 94%; 2.55 g. of $W(NO)_2Cl_2(C_7H_9N)_2$, 96%.

$Mo(NO)_2Cl_2(C_5H_5N)_2$.—$Mo(NO)_2Cl_2$ (1.15 g., 0.050 mole) was dissolved in pyridine (15 ml.) under nitrogen, at room temperature without effervescence. Pentane was added and the solution cooled. On standing, small green crystals were precipitated; yield 1.37 g., 71%.

$[Mo(NO)_2Cl_4][(C_6H_5)_4As]_2$ and $[W(NO)_2Cl_4][(C_6H_5)_4As]_2$.—A solution of tetraphenylarsonium chloride (4.2 g., 0.01 mole) in acetonitrile (10 ml.) was added, under nitrogen, to a solution of $Mo(NO)_2Cl_2$ (1.15 g., 0.005 mole) or $W(NO)_2Cl_2$ (1.60 g., 0.005 mole) in the same solvent (20 ml.). The solution immediately became lighter in color. The solvent was removed under vacuum. The yellow-green residual solid was recrystallized from an acetone–alcohol mixture. Yields: 3.96 g. of Mo compound, 74%; 4.95 g. of W compound, 86%.

$Mo(NO)_2Cl_2(C_6H_{11}NH_2)_2$.—Cyclohexylamine (1.0 g., 0.01 mole) was added to a solution of $Mo(NO)_2Cl_2$ (1.15 g., 0.005 mole) in acetone (20 ml.). The solvent was removed under vacuum, leaving a yellow-green residue of $Mo(NO)_2Cl_2(C_6H_{11}NH_2)_2$. Attempts to recrystallize the product from a variety of solvents always resulted in some decomposition and were therefore abandoned.

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A Spectrophotometric Study of Molybdenum(V) and Molybdenum(VI) in Hydrobromic Acid[1]

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Ultraviolet spectrophotometry was used to study the species of Mo(V) and Mo(VI) present in hydrobromic acid solutions. An investigation of the equilibrium between Mo(VI), Mo(V), and Br_3^- in 8.6 *M* HBr led to the conclusion that both the Mo(V) and Mo(VI) species are dimeric. Each of the following compounds of Mo(V) was prepared and its characteristic spectrum determined in inert solvents: $(NH_4)_2MoOBr_5$, $(C_9H_8N)MoOBr_4$, and $MoO(OH)_2Br_2\cdot 4H_2O$. The spectra of solutions of Mo(V) in aqueous HBr, 1.0–8.6 *M* in concentration, can be interpreted in terms of the presence of four Mo(V) species, all of which are dimeric. In the highest HBr concentration $(MoOBr_4^-)_2$ is the predominant form, with no spectral evidence for the presence of $MoOBr_5^{2-}$.

A number of workers have made investigations of the species of Mo(V) existing in hydrochloric acid solution. Among the variety of methods employed in these studies have been spectrophotometric,[3–6] magnetic,[7–9] and potentiometric[3] measurements. The general conclusions to be reached from these studies are: (1) monomeric $MoOCl_5^{2-}$ is the predominant species in high (>10 *M*) concentration; (2) at intermediate HCl concentrations (2–7 *M*) two or more dimeric forms exist in equilibrium; (3) at low HCl concentrations the situation is less clear, and tetramers are possibly present.

Investigations of solutions of Mo(V) in hydrobromic acid have been few, although several oxybromo compounds of Mo(V) have been isolated from such solutions.[10–13] No work has been reported on the nature of solutions of Mo(VI) in hydrobromic acid.

In the present work a spectrophotometric investigation of the species of Mo(V) existing in hydrobromic acid is reported. Known compounds of molybdenum(V) and bromine were prepared and their spectra determined in inert solvents. A comparison of these spectra with the spectra of solutions of Mo(V) in aqueous HBr made it possible to identify some of the species in solution. In preliminary experiments it was observed that Mo(VI) reacts with moderately concentrated solutions of HBr to form an equilibrium mixture of Mo(V), Mo(VI), and Br_3^-. Certain features of this equilibrium were also investigated.

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(2) Taken from a thesis submitted by Joe Frank Allen in partial fulfillment of the requirements for the Ph.D. degree, Sept., 1962.

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Experimental

Reagents and Materials.—The aqueous hydrobromic acid used in these investigations was distilled from a mixture of powdered red phosphorus and A.R. 47% hydrobromic acid, yielding constant boiling acid at 8.66 *M* concentration. This acid was stored in a polyethylene bottle and was found to be stable for at least 2 weeks, as noted by the lack of an absorption peak at about 265 mμ. The primary impurity in aged HBr is the tribromide ion, Br_3^-, which results from air oxidation and which shows an absorption maximum at 265 mμ.

The lithium bromide solutions were prepared from A.R. $LiBr \cdot xH_2O$. These solutions were passed through a Dowex-1 ion-exchange resin to remove traces of colored impurities, probably small amounts of transition metal bromides. The resulting LiBr solutions were spectrophotometrically clear in the visible and near-ultraviolet regions of the spectrum.

All other chemicals used were C.P. or A.R. grade. The organic solvents showed no absorbance in the visible and near-ultraviolet regions of the spectrum, either before or after shaking with aqueous HBr.

Preparation of Compounds.—$(NH_4)_2MoOBr_5$ was prepared by dissolving 15 g. of ammonium paramolybdate, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, in 100 ml. of fuming HBr. The solution was evaporated on a hot plate until dark crystals began to appear. The solution was then allowed to cool and the dark crystals were filtered through a sintered glass filter. The solid was then redissolved in a minimum of hot fuming HBr and allowed to recrystallize, yielding brown crystals which darkened rapidly upon exposure to air. They were dried over H_2SO_4 and KOH in a vacuum desiccator. The appearance of this solid was in agreement with the description given by Weinland and Knoll[10] for the compound of formula $(NH_4)_2MoOBr_5$. *Anal.* Calcd. for $(NH_4)_2MoOBr_5$: NH_3, 6.5; Mo, 17.5; Br, 72.9. Found: NH_3, 6.5; Mo, 17.0; Br, 72.9.

$(C_9H_8N)MoOBr_4$ was prepared using a variation of the method described by Weinland and Knoll.[10] MoO_3 (20 g.) was added to 100 ml. of fuming HBr. Heating was required to effect solution and to accelerate the reduction of the Mo(VI) to Mo(V) by the hydrobromic acid. Dropwise addition of a solution of 10 g. of quinoline in fuming HBr to the hot solution, with constant stirring, gave an immediate formation of dark red, needle-like crystals. These were recrystallized from fuming HBr, yielding a set of bright red needles which turned orange upon drying over H_2SO_4 and KOH in a vacuum desiccator. These crystals correspond to those described by earlier investigators.[10,12] *Anal.* Calcd. for $(C_9H_8N)MoOBr_4$: Mo, 17.1; Br, 56.9. Found: Mo, 17.4; Br, 57.3.

$MoO(OH)Br_2 \cdot 4H_2O$ was prepared by heating 20 g. of MoO_3 in contact with fuming HBr until solution was effected. After the solution was allowed to evaporate at room temperature for about 1 month, a dark solid precipitate was formed. The prism-like solid was recrystallized from HBr, requiring several days for reprecipitation to occur, with no change in the appearance of the solid. Attempts to dry the solid over H_2SO_4 and KOH led to the formation of a "molybdenum blue." After air drying for 2 days on a fritted glass plate, the solid was found to be dark only on the exposed surface, with the freshly crushed solid having a brown appearance which quickly darkened upon exposure to air. Analysis was made on large crystals so that relatively little of the dark surface was used. This compound is similar to that reported by Weinland and Knoll as $MoO(OH)Br_2 \cdot 1.5H_2O$, which was reported to be hygroscopic. The air drying procedure possibly explains the higher number of water molecules and the nonhygroscopic nature of the presently reported compound. *Anal.* Calcd. for $MoO(OH)Br_2 \cdot 4H_2O$: Mo, 26.6; Br, 44.4. Found: Mo, 26.7; Br, 45.6.

Absorption Spectra Measurements.—The absorption spectra were taken on a Beckman Model DU spectrophotometer and on a Beckman Model DK-1 recording spectrophotometer. The Model DU was used at specific wave lengths for gathering the more accurate data required for the calculations reported, while the curves covering a wide range of the spectrum were obtained using the Model DK-1. All measurements were made at 25°. Three sets of silica absorption cells were used, allowing a choice of 10, 1, and 0.1 cm. path length. The 0.1-cm. path length was obtained by inserting matched 0.9-cm. silica plugs into the 1-cm. cells. The values of absorbance reported are for a 1-cm. light path unless otherwise specified.

The Beer–Lambert law expressing the relationship between the absorbance, *A*, and the molarity, *C*, of an absorbing species is $A = \epsilon Cd$, in which d is the path length of the cell and ϵ is the molar absorbancy index of the absorbing species. Because of the marked tendency for molybdenum to appear in condensed forms, and because the extent of condensation is often unknown, the true molarity may be unknown. For this reason it is convenient to use the modified equation $A = \alpha fd$, where f is the formal concentration of molybdenum; *i.e.*, the number of moles of molybdenum atoms per liter of solution, and the proportionality constant α may be called the formal absorbancy index.

Since it has become standard practice to use the symbol [X] to stand for the "molar concentration of X," it would be convenient to have a similar symbol for the "formal concentration of X." For this purpose $\{X\}$ will be used.

Analytical Methods.—Bromide was determined by potentiometric titration with a standard $AgNO_3$ solution of the sample dissolved in cold 1 *M* HNO_3. The stock Br_2 solution was analyzed by reaction with KI to give an I_2 solution, the latter being used to titrate weighed portions of As_2O_3. Analysis for ammonia in the ammonium salt was performed by the standard volatilization procedure.

A spectrophotometric method which could be utilized for analysis of Mo(V) and/or Mo(VI) was developed. The method is based on the known absorption characteristics of solutions of Mo(V) in hydrochloric acid.[4-6] In analyzing solid compounds an accurately weighed sample of about 0.3 g. was dissolved in 20 ml. of 6.5 *M* HCl and placed into a 50-ml. volumetric flask. One ml. of 8.6 *M* HBr was added, so that by swamping the bromide that was present in the unknown sample all the samples would contain the same bromide concentration, and 6.5 *M* HCl was used to dilute to the mark. The absorbance was then measured at 700 mμ using 1-cm. Pyrex cells and a Beckman Model DU spectrophotometer with a slit width of 0.6 mm. The concentration of Mo(V) was determined from a previously prepared graph of known Mo(V) concentration plotted against absorbance. (The graph is necessary because these solutions show a slight deviation from the Beer–Lambert law.) To determine the total molybdenum concentration, 0.25 ml. of 6.5 *M* HCl saturated with hydrazine was added to the flask. The solution was then heated moderately until effervescence ceased, or, alternatively, the solution was allowed to stand for 12 hr. at room temperature. The hydrazine reduces the Mo(VI) to Mo(V), evolving nitrogen. The solution was then cooled, and the absorbance measured at 700 mμ as before. Procedures for analyzing solutions were analogous.

Results

Spectra of Compounds.—In water and many other solvents the compounds react on dissolving. It was assumed that by trying a variety of solvents with a given compound that a few of the solvents would either be inert or react only slowly and that solutions in these solvents would give markedly similar, if not identical, absorption spectra.

Fresh solutions of $C_9H_8NMoOBr_4$ in N,N-dimethylformamide, acetonitrile, and chloroform gave essentially the same spectra characterized by a broad weak band at about 700 mμ, a shoulder at 480 mμ, and peaks at 414, 380, and 305 mμ. The 305 mμ peak is due to the quinolinium ion, $C_9H_8N^+$; the remainder are characteristic of $MoOBr_4^-$. Some decomposition of the $MoOBr_4^-$ ion in ethyl acetate was indicated by the

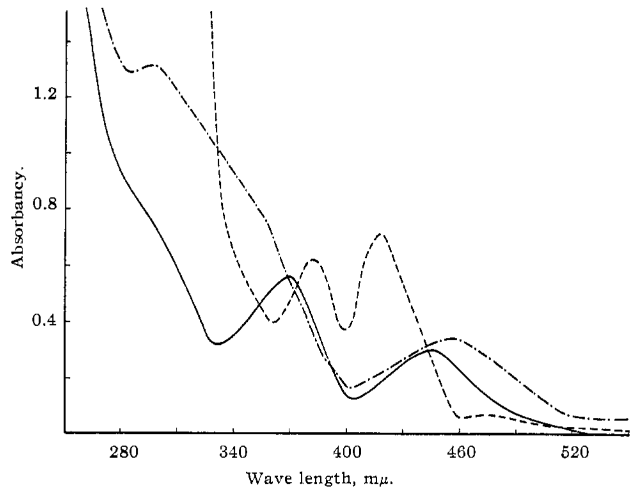

Fig. 1.—Ultraviolet and visible spectra of molybdenum(V) bromide compounds in organic solvents at 2 × 10^{-4} *M* concentration: ———, $MoO(OH)Br_2 \cdot 4H_2O$ in ethyl acetate; – – – –, $C_6H_8NMoOBr_4$ in acetonitrile; –·–·–·, $(NH_4)_2MoOBr_5$ in dimethyl sulfoxide.

spectrum, since the peaks were generally of lower intensity, the 380 mμ peak was displaced to 376 mμ, and it had an intensity greater than the 414 mμ peak. Such a solution was stable for days. Addition of excess bromide ion, as tetraethylammonium bromide, to the ethyl acetate solution caused the appearance of a spectrum like that in the other solvents. In the N,N-dimethylformamide solutions the $MoOBr_4^-$ absorption peaks decreased with time, disappearing in a few hours. This decrease could not be reversed by the addition of excess Br^-. The acetonitrile and chloroform solutions were stable over the period of a few hours required to make the studies.

The brown solid $MoO(OH)Br_2 \cdot 4H_2O$ displayed similar spectra in the solvents chloroform and ethyl acetate. This compound shows a broad band at about 670 mμ and a peak at 370 mμ. A second broad band appears at 460 mμ in chloroform, and at about 445 mμ in ethyl acetate. There is no absorption peak in the 414 mμ region for either solution. These spectra did not change with time. Addition of tetraethylammonium bromide to the ethyl acetate solution converted the spectrum to one essentially identical with that described above for the $MoOBr_4^-$ ion.

It was difficult to obtain a suitable solvent in the case of $MoOBr_5^{2-}$. Addition of solid $(NH_4)_2MoOBr_5$ to diethyl ether, ethyl acetate, N,N-dimethylformamide, and acetonitrile gave some insoluble NH_4Br and solutions whose spectra appeared to be mixtures of $MoOBr_4^-$ and $MoO(OH)Br_2$. The compound $(NH_4)_2MoOBr_5$ dissolved in dimethyl sulfoxide with no rapid decomposition apparent; the spectrum of this solution showed a broad weak band at 770 mμ, broad absorption at 460 mμ, and a large peak at about 300 mμ with a shoulder at about 350 mμ. The peaks dropped uniformly with time over a period of hours, with no change in relative intensities, until they had disappeared at the end of 24 hr. The view that the spectrum in dimethyl sulfoxide is that of $MoOBr_5^{2-}$ is supported by the fact that a KBr pellet containing $(NH_4)_2MoOBr_5$ showed absorption bands at 470 and 300 mμ.

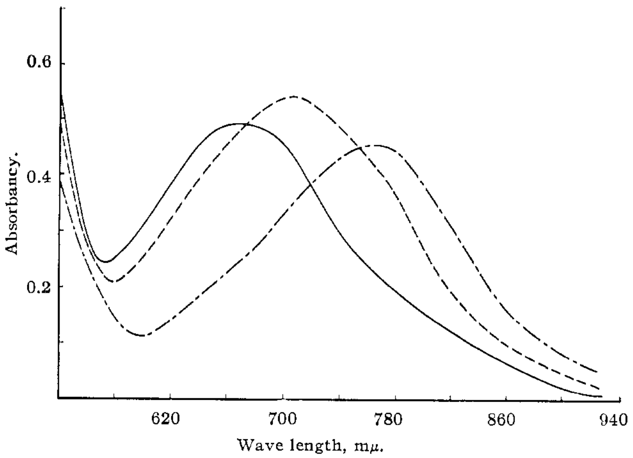

Fig. 2.—Visible and near-infrared spectra of molybdenum(V) bromide compounds in organic solvents at 3 × 10^{-2} *M* concentration: ———, $MoO(OH)Br_2 \cdot 4H_2O$ in chloroform; – – – –, $C_6H_8NMoOBr_4$ in N,N-dimethylformamide; –·–·–·, $(NH_4)_2MoOBr_5$ in dimethyl sulfoxide.

Recently English workers[13] have reported the spectra of compounds containing $MoOBr_5^{2-}$ and $MoOBr_4^-$. They report maxima in the diffuse reflectance spectra of salts containing $MoOBr_5^{2-}$ at 470 and 710 mμ. They report maxima for $C_5H_6NMoOBr_4$ dissolved in liquid SO_2 at 440 and 675 mμ. Comparison with our results suggests that some solvolysis has occurred in this last case.

Representative spectra of the compounds measured are shown in Fig. 1 and 2. It is assumed that if these species (or ones very similar to them) are present in aqueous hydrobromic acid the spectra should be similar to those shown. In solutions containing more than one species changes in the region 350–450 mμ would be the most significant.

Molybdenum(V)–Molybdenum(VI) Equilibrium in Hydrobromic Acid.—Solutions 2 × 10^{-4} *F* in molybdenum(VI) were prepared in HBr of various concentrations from a stock solution of ammonium paramolybdate in water. The spectra were found to change with time, becoming stable in about 5 days. The 8.6 *M* HBr solution showed a large peak at about 265 mμ, a shoulder at 290 mμ, maxima at 376 and 414 mμ, and a plateau at 470 mμ. The 414 mμ peak was about 30% greater than that at 376 mμ. At higher concentrations of molybdenum (up to about 5 × 10^{-3} *F*) and using 10-cm. cells, a broad band was observed at 700 mμ which was much weaker than the other bands. The absorption at 265 mμ is due to the tribromide ion,[14] and the other maxima indicate the $MoOBr_4^-$ ion. The intensity of the absorption is such that not all the Mo can be present as $MoOBr_4^-$, and since it will be shown later that there is no evidence of Mo(V) species other than $MoOBr_4^-$ in 8.6 *M* HBr, the conclusion is drawn that some Mo(VI) remains. However, none of the

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TABLE I

EQUILIBRIUM CONSTANTS FOR Mo(V)–Mo(VI) EQUILIBRIUM IN 8.6 *M* HBr WITH Br_3^- ADDED

Initial $[Br_3^-] = 1.83 \times 10^{-3}$ *M;* Temperature 25°

			$K' \times 10^3$		$K' \times 10^6$	K'
$\{Mo\}_{total} \times 10^3$	A	$\{Mo(V)\} \times 10^3$	$n = 1$ $m = 1$	$n = 2$ $m = 2$	$n = 1$ $m = 2$	$n = 2$ $m = 1$
5.00	0.436[a]	2.57	3.5	3.3	8.5	1.4
1.09	0.245[b]	0.635	4.2	3.0	1.9	6.6
0.872	0.195[b]	0.505	3.9	2.8	1.4	7.8
0.545	0.123[b]	0.319	4.0	2.8	0.89	12.4
0.436	0.933[c]	0.242	3.0	2.4	0.59	12.6
0.200	0.432[c]	0.112	3.0	2.4	0.27	27
0.100	0.213[c]	0.055	2.8	2.3	0.13	51

[a] 700 mμ, 10-cm. cell. [b] 414 mμ, 0.1-cm. cell. [c] 414 mμ, 1-cm. cell.

bands in the observable spectrum can be attributed to Mo(VI).

A study of this equilibrium was made to yield information on the nature of the species involved. In its most general form the equation for the reaction can be written as

$$\frac{2}{m}\mathrm{Mo(VI)}_m + a\mathrm{H}^+ + b\mathrm{Br}^- \rightleftharpoons \frac{2}{n}(\mathrm{MoOBr_4^-})_n + \mathrm{Br_3^-} + c\mathrm{H_2O} \quad (1)$$

where $Mo(VI)_m$ indicates a species containing m atoms of Mo(VI) and unknown numbers of H, O, and Br atoms. The equilibrium constant is given by

$$K = \frac{[(\mathrm{MoOBr_4^-})_n]^{2/n}[\mathrm{Br_3^-}]}{[\mathrm{Mo(VI)}_m]^{2/m}[\mathrm{H^+}]^a[\mathrm{Br^-}]^b}$$

The values of m and n were investigated in experiments in which the hydrobromic acid concentration was maintained constant at 8.6 *M;* under these conditions

$$K(n)^{2/n}\left(\frac{1}{m}\right)^{2/m} [\mathrm{H^+}]^a[\mathrm{Br^-}]^b = K' = \frac{\{(\mathrm{MoOBr_4^-})_n\}^{2/n}[\mathrm{Br_3^-}]}{\{\mathrm{Mo(VI)}_m\}^{2/m}}$$

Using the absorbance at 414 mμ ($\alpha = 3860$) or at 700 mμ ($\alpha = 17.0$) as a measure of the $(MoOBr_4^-)_n$ concentration

$$\{(\mathrm{MoOBr_4^-})_n\} = \frac{A}{\alpha d}$$

$$\{\mathrm{Mo(VI)}_m\} = f - \frac{A}{\alpha d}$$

$$[\mathrm{Br_3^-}] = X + \frac{1}{2}\frac{A}{\alpha d}$$

where f is the total formal molybdenum concentration and X is the concentration of added Br_3^-. It follows then that

$$K' = \frac{\left(\frac{A}{\alpha d}\right)^{2/n}\left(X + \frac{1}{2}\frac{A}{\alpha d}\right)}{\left(f - \frac{A}{\alpha d}\right)^{2/m}}$$

In one set of equilibrium studies an aliquot of a stock solution of Br_3^- in 8.6 *M* HBr was added to the solution of Mo(VI) in HBr to give $X = 1.83 \times 10^{-3}$. The spectra of these solutions were measured after allowing several days for equilibration. The values of K' calculated for various values of m and n are shown in Table I. It is concluded that $m = n$.

Determination of the values of m and n is best accomplished using solutions which contain no added Br_3^-. The results of such a series are given in Table II. It can be seen that the data are best satisfied by $n = m = 2$. The average value for the equilibrium constant K' taken over all the data listed in Tables I and II is $K' = (2.3 \pm 0.6) \times 10^{-3}$.

TABLE II

EQUILIBRIUM CONSTANTS FOR Mo(V)–Mo(VI) EQUILIBRIUM IN 8.6 *M* HBr; TEMPERATURE 25°

			$K' \times 10^3$	
$\{Mo\}_{total} \times 10^3$	A	$\{Mo(V)\} \times 10^3$	$n = m = 2$	$n = m = 1$
2.50[d]	0.629[a]	1.63	1.5	2.8
2.50	0.280[b]	1.65	1.6	3.0
2.50	0.656[a]	1.70	1.8	3.8
2.00[d]	0.601[a]	1.56	2.7	9.6
2.00	0.239[b]	1.41	1.7	3.9
2.00	0.593[a]	1.54	2.5	8.4
1.00	0.298[a]	0.77	1.3	4.4
1.00[d]	0.336[a]	0.87	2.9	19
1.00	0.137[b]	0.81	1.7	7
0.200	0.740[c]	0.192	2.2	51
0.100	0.375[c]	0.097	1.7	59

[a] 414 mμ, 0.1-cm. cell. [b] 700 mμ, 10-cm. cell. [c] 414 mμ, 1-cm. cell. [d] Single equilibration.

With the aim of gaining some insight into the composition of the Mo(VI) species present in these solutions, some experiments were performed to determine the coefficients in eq. 1. Measurements to determine a were made by maintaining the bromide ion concentration at 8.6 *M*, while varying the hydrogen ion concentration from 6.86 to 8.24 *M*. Mixtures of LiBr and HBr were used in these experiments. These experiments indicated a value of 3 for a.

Measurements to determine b were made by maintaining the hydrogen ion concentration at 8.3 *M*, while varying the bromide ion concentration from 4.85 to 7.28 *M*. Mixtures of HBr and $HClO_4$ were used in these experiments. The results indicated the unrealistic value of -8 for b. The major complication here is

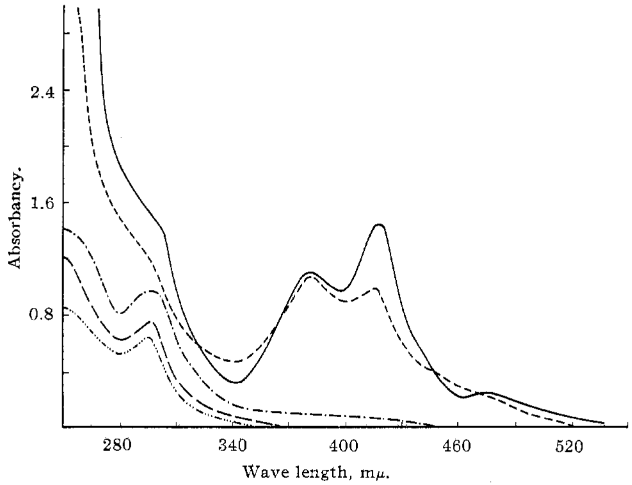


Fig. 3.—Spectra of 4 × 10^{-4} *M* molybdenum(V) in hydrobromic acid solutions: ———, 8.6 *M* HBr; - - - -, 6.5 *M* HBr; –·–·–·, 5.0 *M* HBr; — —, 3.5 *M* HBr; –··–··, 1.1 *M* HBr.

that more than one Mo(V) species is present in this concentration range, and the same may be true of Mo(VI). The lack of constancy of the activity of water and of the activity coefficients of the ions is an additional complication. Since these factors exist, although to a smaller extent, in the determination of *a*, one can have little confidence in $a = 3$.

Molybdenum(V) in Hydrobromic Acid.—A series of investigations was made concerning the Mo(V) species which exist in aqueous HBr. A stock solution of Mo(V) was prepared by dissolving ammonium paramolybdate in 8.6 *M* HBr, adding hydrazine, and heating until nitrogen was no longer expelled, indicating that the reduction was completed. From the stock were prepared solutions of varying Mo(V) and HBr concentrations, whose spectra are shown in Fig. 3 and 4. These spectra can best be interpreted in terms of four Mo(V) species, some of which can be identified by comparison with the spectra of solutions of pure compounds.

The spectrum of the 8.6 *M* HBr solution has peaks at 380, 414, 475, and 700 mμ, distinctly like that displayed by solutions of $(C_9H_8N)MoOBr_4$ in inert solvents. Since it has already been demonstrated that Mo(V) is dimeric in such HBr solutions, the predominant form of Mo(V) must be $(MoOBr_4^-)_2$. Excess bromide, in the form of LiBr, was added to this solution in an attempt to convert some of the Mo(V) to $MoOBr_5^{2-}$. However, there was no difference in the spectra of solutions 2.2 *M* in LiBr and 8.6 *M* in HBr as compared to those which were 8.6 *M* in HBr and contained no LiBr. This establishes the fact that $MoOBr_5^{2-}$ does not exist in significant amounts in aqueous HBr solutions.

The 6.5 *M* HBr solution shows deviation from the spectrum of $(MoOBr_4^-)_2$, which will be designated as species I for convenience. The 475 mμ peak shifts to shorter wave lengths and becomes a shoulder; there is a decrease in the 414 mμ peak and the 376 mμ peak decreases only slightly but broadens on the short wave length side. This spectrum shows that I is in equilibrium with a species II, which must have a spectrum like that of the compound $MoO(OH)Br_2$.

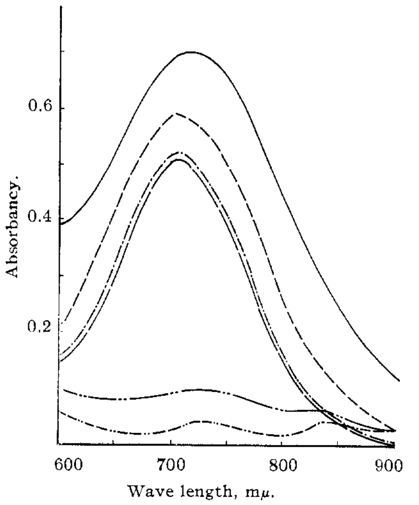


Fig. 4.—Spectra of 2.5 × 10^{-3} *M* molybdenum(V) in hydrobromic acid solutions: — —, 8.5 *M* HBr; –·–·–, 7.7 *M* HBr; - - - -, 6.8 *M* HBr; ———, 6.0 *M* HBr; –··–··, 5.1 *M* HBr; –···-, 4.3 *M* HBr.

In the solutions 1–5 *M* in HBr only a trace of the complexes absorbing in the 350–500 mμ region remain, the spectra showing instead a large maximum at 295 mμ, attributed to a species III. This maximum decreases as the acid concentration decreases. It is concluded that species III is in equilibrium with a small amount of II and a fourth substance IV in the 3–5 *M* HBr solutions and that III and IV coexist in the low acid range.

The spectra in the 700–900 mμ region (Fig. 4) provide further evidence. In 8.6 *M* HBr the peak is at 700 mμ, but as the acid concentration is dropped to 6.0 *M*, the peak rises, broadens, and shifts to about 720 mμ, showing a small shoulder at about 840 mμ. A further decrease in acid concentration leads to a very sharp decrease in the 720 mμ peak, which shifts to 740 mμ, and there is the presence of a distinct but very weak absorption band at 840 mμ (extinction coefficient of about 1). Both the 840 mμ peak and the remnant of the 740 mμ peak fall as the HBr concentration is decreased below 5 *M*, with the 740 mμ band showing the greater drop. These variations are quite satisfactorily explained in terms of the existence of four species. Species I absorbs at 700 mμ and is the only species present in 7.8–8.6 *M* HBr; however, in 6–7.8 *M* HBr this ion coexists with species II which absorbs at 740 mμ, with an extinction coefficient greater than that of species I at 700 mμ. Even in 6 *M* HBr there is evidence for the formation of species III, which has the very weak absorption maximum at about 840 mμ. In solutions of less than 6 *M* HBr the drop in the 740 mμ peak indicates only a trace of II in these solutions. As the acid concentration decreases further, both the 740 and 840 mμ peaks drop, indicating the formation of substance IV which does not absorb in this region of the spectrum.

An estimation of the relative concentrations of each

TABLE III

BEER–LAMBERT LAW DATA FOR THE Mo(V) SYSTEM

	6.2 *M* HBr				5.2 *M* HBr		1.0 *M* HBr	
$\{Mo(V)\}_{total}$	A_{414}	α_{414}	A_{376}	α_{376}	A_{296}	α_{295}	A_{295}	α_{295}
5×10^{-5}	0.150	3000	0.142	2840	0.124	2480	0.083	1660
1×10^{-4}	0.318	3180	0.294	2940	0.242	2420	0.162	1620
2×10^{-4}	0.634	3170	0.594	2970	0.482	2410	0.326	1630
4×10^{-4}	1.22	3050	1.15	2870	0.955	2390	0.646	1620

of the four species in various HBr concentrations is presented in Fig. 5.

Solutions 6.2, 5.2, and 1.0 *M* in HBr, representing regions of transition between species, were examined for adherence to the Beer–Lambert law (Table III) by varying the total Mo(V) concentration. The conclusion is drawn that I, II, III, and IV must all have the same degree of condensation; and since I, $(MoOBr_4^-)_2$, has been shown to be dimeric, then the other species must also be dimeric.

In solvent extraction experiments, Mo(V) is extracted into ethyl acetate or isopropyl ether, and in the organic phase displays the spectrum of species II. There is negligible extraction into carbon tetrachloride or chloroform. On this basis it is reasonable that species II be formulated as an anion, with $[MoO(OH)_2Br_2^-]_2$ as a possibility.

Extraction studies made from 5 and 1.1 *M* HBr solutions indicated no extraction of species III, suggesting that it is cationic. A possibility is $[Mo_2O_3Br_2(H_2O)_6]^{2+}$, in analogy to the species $Mo_2O_3Cl_2^{2+}$ suggested by Souchay and Simon[4] for the Mo(V)–HCl system. Since the extraction evidence is not conclusive, other possibilities are a neutral species, such as $[Mo_2O_2Br_2(OH)_4(H_2O)_2]$, or an anionic species, such as $[Mo_2O_2Br_2(OH)_6]^{-2}$.

Substance IV would likely be a bromide-free cation, as suggested by other investigators for dilute acid solutions.[3–5]

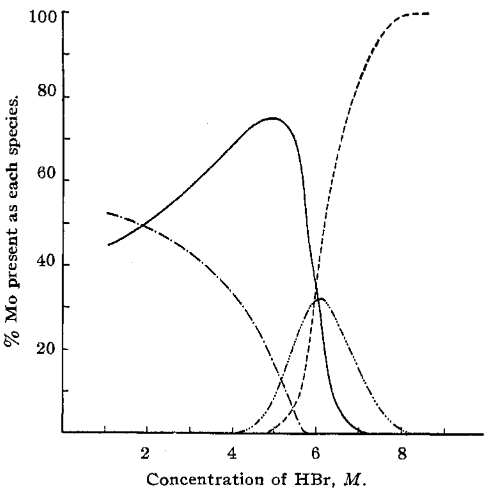
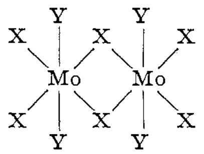


Fig. 5.—Relative amounts of molybdenum(V) species in hydrobromic acid solutions: – – – –, species I; –··–··, species II; ———, species III; –·–·–·, species IV.

Discussion

This study demonstrates the marked tendency for dimerization of Mo(V) in its bromo complexes, a tendency already noted in studies of the oxychloro complexes. Although dimerization through a single oxo-bridge has been suggested for one of the oxychloro complexes,[6] there is evidence to suggest that double bridges exist frequently. Assuming that Mo(V) has coordination number six, the known compounds[6,12,15] $C_5H_6N(MoOBr_4)$, $C_9H_8N(MoOBr_4)$, $C_5H_6N(MoO_2Cl_2 \cdot H_2O)$, and $Mo_2O_4(OH)Cl \cdot 4H_2O$ can only be formulated readily in terms of doubly-bridged dimers.

The known structure of $MoCl_5$ provides a likely model for the doubly-bridged dimers. Although electron diffraction studies[16] of $MoCl_5$ in the vapor state show that it is a monomer with the structure of a trigonal bipyramid, X-ray studies[17] reveal that it exists as a dimeric molecule in the solid state. Basically the structure is



where the Mo atoms and the six Cl atoms labeled X lie in one plane, while the two Mo atoms and the Cl atoms labeled Y lie in a second plane perpendicular to the first. The same basic structure has been suggested[18] for the $[Mo_2O_4(NCS)_6]^{-4}$ ion. In structures of this type, if the bridging groups are small enough to bring the Mo atoms within bonding distance, there may be a decrease in or a loss of the paramagnetism generally associated with Mo(V) ions.

Distortion from perfect octahedral arrangement about each Mo in $(MoCl_5)_2$ results from the repulsion of Cl atoms on the same Mo.[17] Since steric strain exists in $(MoCl_5)_2$, it will clearly be even more important when the larger Br atom is present. In attempting to evaluate the steric strain in these bromo and related chloro dimers we have assumed the following bond distances and van der Waals radii (Å.): Mo–O, 2.00; Mo–Cl, 2.25; Mo–Br, 2.50; O, 1.40; Cl, 1.80; Br, 1.95.

The ion $MoOBr_5^-$ would be expected to be essentially octahedral. Use of the numerical values above suggests that distortion will result because of Br–Br repulsion, leading to bond angles other than 90°.

The experimental evidence for the $Mo_2O_2Br_8^{2-}$ dimer

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[15] R. G. James and W. Wardlaw, *J. Chem. Soc.*, 2145 (1927).

[16] R. V. G. Ewens and N. W. Lister, *Trans. Faraday Soc.*, **34**, 1358 (1938).

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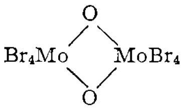
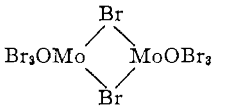
is quite strong. Because of the unambiguous stoichiometry of the isolated compound, a dimeric structure with two bridging groups seems to be the most plausible; either

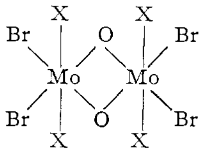


or



If bridging is by bromines the steric strain will probably be relieved principally by lengthening of the central Mo–Br bonds, without much additional distortion. If the bridging is by oxygen atoms it would appear difficult to maintain bond angles of 90° about the Mo atoms and the Mo–O bonds would probably be unusually long. In either case the Mo–Mo distance would undoubtedly be too great to lead to a decrease in the magnetic moment. Hence the magnetic moments of 1.77–1.78 reported by Klemm and Steinberg[19] for two salts of the type $M(MoOBr_4)$ do not rule out the dimeric structure.

A dimer with the formula



where X is either OH or O might not be subjected to such steric effects and thus might be diamagnetic. The existence of both paramagnetic and diamagnetic dimers might then be expected. Such has actually been observed in the chloro complexes of Mo(V).[7-9]

It is the consensus of workers on the similar system in HCl that monomeric $MoOCl_5^{2-}$ is the predominant form in high HCl concentrations and that a series of dimers appears at lower concentrations. The absence of significant amounts of $MoOBr_5^{2-}$ in the HBr solutions is the most marked difference between the bromo and chloro systems.

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[19] W. Klemm and H. Steinberg, *Z. anorg. allgem. Chem.*, **227**, 193 1936).

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The Absorption Spectra of Uranium(V) Compounds[1]

BY D. G. KARRAKER

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The absorption spectra of the uranium(V) ion in CCl_4 solutions of $UCl_5 \cdot SOCl_2$ and $[U(OC_2H_5)_5]_2$ were measured, and energy levels were assigned on the basis of a $5f^1$ configuration for the U(V) ion. Comparison of these energy levels with the theoretical levels for a $5f^1$ configuration was satisfactory, and the spin–orbit coupling constant for U(V) was calculated to be 1900 cm.$^{-1}$. The shifts in the energy levels between the two compounds were interpreted to result from a 30% stronger field on the U(V) ion in $[U(OC_2H_5)_5]_2$.

Introduction

The uranium(V) ion has one unpaired electron, probably in a $5f^1$ configuration, and is thus isoelectronic with Pa(IV) and Np(VI). The optical spectra and paramagnetic resonance of both Pa(IV) and Np(VI) have been previously measured and interpreted.[2-7] Similar measurements for U(V) would also be of interest, but are complicated by the difficulty of preparing U(V) compounds that have a known symmetry and are chemically stable. Absorption spectra of alkali metal–U(V) fluorides has been recently reported by Penneman, *et al.*[8,9] A partial interpretation of the spectra of these compounds has also been proposed.[10] This paper reports the absorption spectra of two U(V) compounds, uranium pentaethoxide and the thionyl chloride complex of uranium pentachloride, and proposes an interpretation of the spectra consistent with the energy levels in a $5f^1$ configuration.

Experimental

Materials. $UCl_5 \cdot SOCl_2$.[11]—$UCl_5 \cdot SOCl_2$ was prepared by refluxing uranium trioxide (20 g.) with an excess of thionyl chloride (300 ml.) for 3 weeks. The solution was filtered to remove unreacted UO_3, and the excess thionyl chloride was removed by distillation at atmospheric pressure, followed by vacuum distillation. The yield was essentially quantitative. *Anal.* Calcd. for $UCl_5 \cdot SOCl_2$: U, 44.6; Cl, 46.5. Found: U, 45.1; Cl, 46.2.

$[U(OC_2H_5)_5]_2$.[12]—Uranium(IV) chloride (19 g., 0.05 mole), dissolved in dry absolute ethanol, was added slowly to an ethanolic solution of sodium ethoxide (13.6 g., 0.20 mole) in a nitrogen

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[1] The information contained in this article was developed during the course of work under contract AT(07-2)-1 with the U. S. Atomic Energy Commission. Presented at the 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April, 1964.

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