comes monophasic.[15] The phases present in this region are anion excess fluorite structures with lattice constants of 5.4704 and 5.4411 Å. for UO_2 and U_4O_9, respectively.[15]

It is apparent, then, that there is a solubility loop in the fluorite region between $PrO_{1.83}$ and $PrO_{2.00}$ below a temperature of at least 350° with a probable transition to a homogeneous system at elevated temperatures. This observation based on the present study apparently explains much of the work of others previously thought to be contradictory. It also appears to be a reasonable extension of the known facts of the PrO_x system, as determined by equilibrium dissociation pressure measurements, and is not at variance with observations on related oxide systems including many of the mixed oxides.

It is not possible from the present study to fix the transition temperature exactly, but it must be above 350°. From the extension of the lower oxide studies and the Nd–Pr system an upper limit of approximately 585° would be expected.

Reasonably complete studies of the oxide systems of cerium and praseodymium and preliminary studies on the oxides of terbium[7,8,16,17] have now been reported. It is of interest to compare the phase relationships' of these lanthanide oxides. Each oxide system changes from a body-centered cubic to a rhombohedral to a face-centered cubic phase as the oxygen content is increased. Similar stable compositions exist in each system, with the major difference being the lack of an intermediate face-centered cubic phase in the cerium system. A given region of any of these systems can be either diphasic or monophasic depending upon the temperature and pressure of the preparation.

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[16] D. J. M. Bevan, *J. Inorg. Nuclear Chem.*, **1**, 49 (1955).

[17] E. Daniel Guth and L. Eyring, THIS JOURNAL, **76**, 5242 (1954).

IOWA CITY, IOWA

[CONTRIBUTION FROM THE CHEMISTRY LABORATORIES OF NORTHWESTERN UNIVERSITY]

Species of Molybdenum(VI) in Hydrochloric Acid[1]

BY H. M. NEUMANN[2] AND NANCY C. COOK

RECEIVED DECEMBER 21, 1956

Ultraviolet spectrophotometry has been applied in a study of the species of Mo(VI) present in hydrochloric acid solutions. Compounds of Mo(VI) containing molybdenum and chlorine in the ratios 1:2, 1:3 and 1:4 have been prepared and their spectra determined in ether solutions. Although all three types display a maximum at 226 mμ, each has a second maximum at longer wave lengths that is characteristic of the particular Mo:Cl ratio. These results have been applied to the analysis of the spectra of solutions of Mo(VI) in hydrochloric acid. The species containing two chlorines is the most important in these solutions, its maximum amount occurring in 6 *M* HCl. At greater acidities a species containing three chlorines becomes important. There is no evidence for species containing a larger number of chlorines. The species containing two chlorines is apparently the one extracted by ethers and bound by anion-exchange resins.

Although molybdenum is most commonly encountered as molybdenum(VI), the aqueous chemistry of this oxidation state is, to a large extent, unknown. The greatest difficulties in working out the details of molybdenum(VI) chemistry arise from the fact that in acidic solution polymerization occurs to form polymolybdates. By using an acid whose anion could become involved in complex formation, one is more likely to find the molybdenum(VI) present in monomeric form, and hence have some chance of identifying the species actually present. The work reported here is based upon the use of hydrochloric acid as the medium and ultraviolet absorption spectrophotometry as the means of studying the composition of the various solutions. This seemed a promising method since any chloro complexes would be expected to have absorption maxima in the ultraviolet region. In addition, several compounds of Mo(VI), containing various numbers of chlorine atoms, have been reported in the literature, and it seemed likely that a comparison of their spectra with those of solutions of Mo(VI) in hydrochloric acid would give information about the species of Mo(VI) present in the acid solutions.

The ultraviolet spectra of the compounds themselves are of interest, since at the present time there is little apparent correlation between the spectra and structure of halo complexes. In part, this is due to insufficient data, so that any additional data from known compounds, as is possible in the molybdenum(VI) case, may ultimately lead to some correlations.

Experimental

Analytical Methods.—Determinations for molybdenum in macro concentration were performed by the method described by Kolthoff and Sandell.[3] The chloride determinations employed the method suggested by Michael and Murphy[4] for chloride in the presence of molybdenum. The determination of the total molybdenum(VI) in ether solutions when the molybdenum concentration was of the order of 10^{-4} *M* was accomplished by completely transferring all the Mo(VI) into an aqueous 6 *M* HCl solution by evaporating a measured aliquot of the ether solution while in contact with the 6 *M* HCl solution, boiling to remove all the ether, and then diluting with additional 6 *M* HCl to a fixed volume. The absorption spectrum of the solution was then measured, and compared with the spectra of solutions of known concentrations in 6 *M* HCl.

Measurements of Absorption Spectra.—All absorption spectra were measured with a Beckman Model DU spectrophotometer using matched, fused silica cells having a light path of 1 cm. The cells were maintained at a constant temperature of 25° by means of a water jacket. The spectra of hydrochloric acid solutions were obtained from 212 to 350

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[1] Taken in part from a thesis submitted by Nancy C. Cook in partial fulfillment of the requirements for the M.S. degree. Presented in part at the Dallas meeting of the American Chemical Society, April, 1956.

[2] School of Chemistry, Georgia Institute of Technology, Atlanta, Georgia.

[3] I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Co., New York, N. Y., 1946, pp. 597–600.

[4] A. Michael and A. Murphy, *Am. Chem. J.*, **44**, 365 (1910).

mμ, and in ether solutions from 218 to 350 mμ. Readings were taken at 2 mμ intervals from 212 to 300 mμ, and at 5 mμ intervals thereafter. The slit width was varied from one wave length to another, but was maintained constant for a given wave length for all solutions in the same solvent.

A stock solution 0.114 *M* in Mo(VI) was prepared in concentrated hydrochloric acid. The solutions to be used for spectral determination were prepared by placing a measured aliquot of the stock solution in a 50-ml. volumetric flask and diluting to the mark with hydrochloric acid of the desired concentration.

The ether solutions used for spectral determination were prepared in the following way. A saturated solution was obtained by contacting the solid compound with anhydrous ether. The solution was then diluted until the optical density reached a reasonable value, and the spectrum then determined. The concentration of the Mo(VI) in the ether was then determined in the way previously outlined.

Preparation of Compounds: MoO_2.—The method of Guichard[5] was used. An approximately 1:1 volume ratio of molybdenum trioxide and ammonium molybdate was pulverized and heated to red heat in a platinum crucible. The molten mass was solidified by pouring it into cold water. The crystals were washed several times with ammonium hydroxide by decantation, then with 6 *M* hydrochloric acid until the hydrochloric acid ceased to be colored red. The crystals had a dark blue color.

MoO_2Cl_2.—The method of Wasmuht[6] was employed for the preparation of molybdenum dioxydichloride. A reaction chamber was constructed of two glass tubes 18 inches long, the smaller of which was $^3/_4$ in. in diameter. The tubes were fitted together tightly with resistance wire wrapped between them, and the ends of the wire connected to a Variac. About 5 g. of MoO_2 was placed inside the tube at the center. One end of the tube was attached to a cylinder of anhydrous chlorine gas, and the other to the receiver, a large-mouthed bottle. The temperature was set at 360° and gradually increased until yellow powder crystals began to be formed rapidly in the receiver. These crystals were yellow in color, were not appreciably hygroscopic, and discolored only very slowly on exposure to air. *Anal.* Calcd. for MoO_2Cl_2; Mo, 46.4; Cl, 37.8. Found: Mo, 46.3; Cl, 37.7.

$MoO(OH)_2Cl_2$.—The general method given by Weinland and Knoll[7] was followed. Molybdic anhydride, which had been dried at 150° for two hours, was used as the starting material. The same reaction tube was used as for the preparation of MoO_2Cl_2. The chamber was heated to 150° at which time approximately 15 g. of the dry MoO_3 was spread inside the inner tube. A cylinder of anhydrous hydrogen chloride was connected to one end of the tube and the gas was allowed to stream slowly over the MoO_3. A large-mouthed bottle was used as the collection vessel. At 150° very little product was formed, so the temperature was increased slowly. At 250° yellow needle-like crystals formed abundantly in the collection vessel. The color of the crystals was like that of MoO_2Cl_2, but the compound was unlike MoO_2Cl_2 in that it was very hygroscopic, and rapidly turned from yellow to blue. Keeping the product in a dry atmosphere, in a vacuum, or in the dark did not prevent the rapid change in color. The blue material formed was similar in behavior to "molybdenum blue" that is formed as the first product in the reduction of molybdate in acid solution. The blue solid could be converted to a yellow form both by treatment with dilute sulfuric acid and with dilute sodium hydroxide. *Anal.* Calcd. for $MoO(OH)_2Cl_2$: Mo, 44.2; Cl, 31.6. Found: Mo, 44.2; Cl, 32.2.

$MoO(OH)Cl_3 \cdot 7H_2O$.—According to Weinland and Knoll,[7] when $MoO(OH)_2Cl_2$ is made into a mush with fuming hydrochloric acid and the mixture warmed with evolution of hydrogen chloride, the mass solidifies to form $MoO(OH)Cl_3 \cdot 7H_2O$. The compound is also formed by saturating with hydrogen chloride gas a solution of $MoO(OH)_2Cl_2$ in fuming hydrochloric acid and evaporating the liquid over sulfuric acid. The latter method was found more satisfactory. Freshly prepared $MoO(OH)_2Cl_2$ was dissolved in concentrated hydrochloric acid. Hydrogen chloride gas was bubbled into this viscous yellow solution for ten minutes and the solution was placed over sulfuric acid in a vacuum desiccator. As the solution decreased in volume over a period of days it also developed a greenish color. After several days light green crystals were formed which were very hygroscopic, and which turned slightly blue on exposure to air. *Anal.* Calcd. for $MoO(OH)Cl_3 \cdot 7H_2O$: Mo, 26.6; Cl, 29.4. Found: Mo, 26.5; Cl, 30.4.

Other Compounds.—Weinland and Knoll[7] have also reported the preparation of $KMoO_2Cl_3 \cdot H_2O$ and $K_2MoO_2Cl_4 \cdot 2H_2O$ by crystallization from solutions containing $MoO(OH)_2Cl_2$, HCl and KCl; the preparation of $(NH_4)_2MoO_2Cl_4 \cdot 2H_2O$ by crystallization from solutions containing $MoO(OH)_2Cl_2$, HCl and NH_4Cl. Compounds were prepared by these methods, and their properties agreed with those reported by Weinland and Knoll, and the molybdenum and chlorine analyses corresponded to the formulas as written above.

Results and Discussion

Spectra of Compounds in Ether.—The spectra of ether solutions of the prepared compounds were measured as previously described. Aqueous solutions could not be used as all the compounds react rapidly when added to water. Although reaction in ether is a possibility, the results indicate that if any reaction occurs it is limited to the loss of coördinated water molecules from the Mo(VI) complex.

The compounds MoO_2Cl_2 and $MoO(OH)_2Cl_2$ were expected to show good solubility in ether; the most concentrated solutions prepared indicate a solubility in the range 0.02–0.03 *M*. The solubility would be expected to be smaller for $MoO(OH)Cl_3 \cdot 7H_2O$, with a further decrease for $KMoO_2Cl_3 \cdot H_2O$, and with extremely small solubility for $K_2MoO_2Cl_4 \cdot 2H_2O$ and $(NH_4)_2MoO_2Cl_4 \cdot 2H_2O$. Because of the method of preparation of the last three compounds, $MoO(OH)Cl_3 \cdot 7H_2O$ is a possible contaminant. Even though its percentage abundance is small, its greater solubility might result in its being the predominant species present in the solution when the solid is contacted with ether. As a result, the spectra obtained from these three solutions must be interpreted with caution.

Spectra representative of these compounds are shown in Fig. 1. All show a maximum at approximately 226 mμ. The spectra of MoO_2Cl_2 and $MoO(OH)_2Cl_2$ are very similar, having in addition to the maximum at 226 mμ a shoulder in the region of 240–250 mμ. Some variations in the spectra were observed for different preparations and solutions of $MoO(OH)_2Cl_2$, and the same behavior was exhibited by solutions of MoO_2Cl_2. There was no change in the wave length of maximum absorption, but the value of the molar absorbancy index at the maximum varied from 5,500 to 6,200. Although the shoulder was more clearly defined in some samples than others the total variation in molar absorbancy index values did not exceed 5% in this region. The cause of these variations may be the varying amounts of water in the solutions, which can change the extent of oxygen coördination to the molybdenum.

The compounds $MoO(OH)Cl_3 \cdot 7H_2O$ and $KMoO_2Cl_3 \cdot H_2O$ do not have the shoulder, but have instead a second maximum at 290 mμ. The spectra of solutions of the compounds $K_2MoO_2Cl_4 \cdot 2H_2O$ and $(NH_4)_2MoO_2Cl_4 \cdot 2H_2O$ were similar to these, except that the second maximum occurred at 310 mμ rather than at 290 mμ.

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[5] M. Guichard, *Ann. chim. phys.*, [7] **23**, 514 (1901).

[6] R. Wasmuht, *Z. angew. Chem.*, **43**, 101 (1930).

[7] E. Weinland and W. Knoll, *Z. anorg. Chem.*, **44**, 81 (1905).

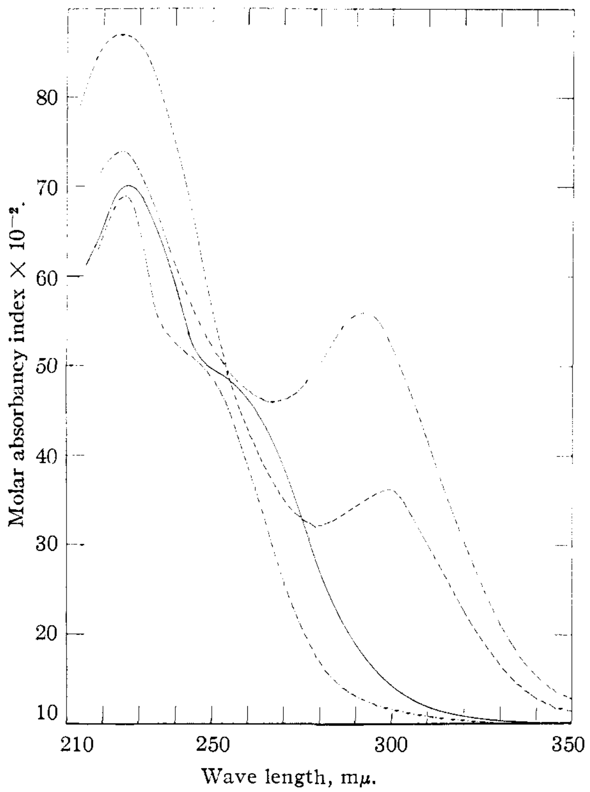

Fig. 1.—Representative spectra of compounds in ethyl ether: —·—·—, compounds containing two chlorines; ---·---, compounds containing three chlorines. Reconstructed spectra of species present in aqueous HCl solutions: ———, the species containing two chlorines; - - - -, the species containing three chlorines.

On the basis of these observations we conclude that all the chlorines appearing in the formula are coördinated to molybdenum, and that the position of the second (*i.e.*, longer wave length) maximum can be used as a measure of the number of coördinated chlorides.

Compounds with a Mo:Cl ratio of 1:2 are characterized by the shoulder at 240–250 mμ; 1:3 compounds by the maximum at 290 mμ. Because of the possibility of $MoO(OH)Cl_3 \cdot 7H_2O$ contributing to the spectra of the 1:4 compounds it cannot be stated that the second maximum for pure 1:4 compounds occurs at 310 mμ; but the maximum certainly must occur at a wave length greater than or equal to 310 mμ.

These spectra are also of interest in connection with the ether extraction of Mo(VI) from hydrochloric acid solutions. The spectra of ether phases obtained by extraction from 3, 6, 7, 8 and 9 *M* hydrochloric acid solutions were measured. All of these ether phases gave spectra characteristic of a compound containing Mo and Cl in the ratio of 1:2. This is in agreement with the ratio obtained by chemical analysis of the ether phase.[8]

Spectra of Hydrochloric Acid Solutions.—Solutions near integral molarities from 1 to 12 *M* were examined. The general characteristics of the spectra are apparent from the selected curves shown in Fig. 2. There is a general similarity to the curves of the pure compounds in ether, but with some shifts in the wave lengths of the maxima. The maximum at 226 mμ is present in the solutions 5 *M* or greater in acidity. The shoulder at 240–250 mμ in the ether solutions, characteristic of compounds containing two chlorines, has shifted to 260–270 mμ. At the highest acidities a second shoulder develops at approximately 300 mμ. This is the region in which we expect a peak due to a species containing three chlorine atoms.

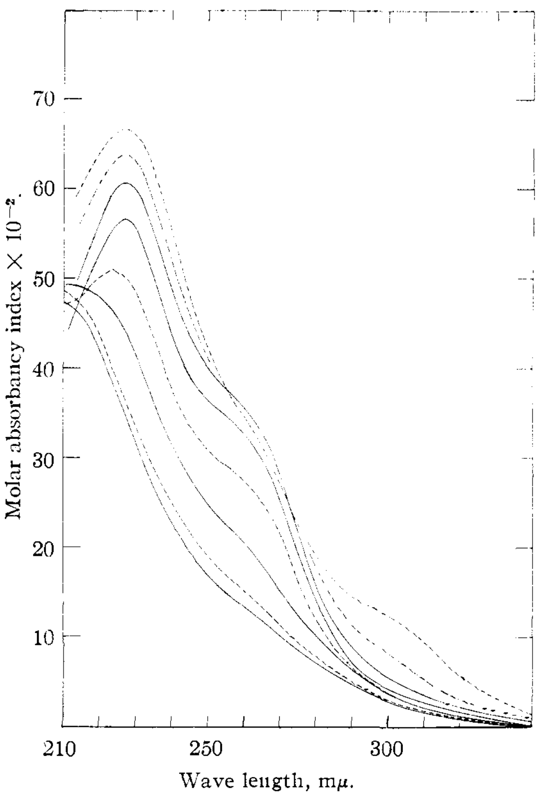

Fig. 2.—Spectra of Mo(VI) in various HCl solutions. Curves in ascending sequence are for the following HCl concentrations: 0.99, 1.98, 2.97, 4.00, 4.94, 6.94, 8.90 (curve only partially shown) and 10.82 *M*.

The spectral changes in hydrochloric acid solutions have been interpreted on the assumption that the species containing two chlorines has an absorption maximum at 226 mμ in addition to the shoulder at 260–270 mμ, while the species containing three chlorines has absorption maxima at 226 and 290–300 mμ. The growth of the absorption maximum at 226 mμ with increasing acidity in the range 5–12 *M*, while that at 260–270 mμ decreases and that at 290–300 mμ increases, quite clearly indicates that the species containing two chlorines has a less intense absorption at 226 mμ than the species containing three chlorines.

It was found possible to resolve these spectra into their component parts by the following method, which is illustrated in Fig. 3. The logarithm of the absorbancy was first plotted *vs.* wave length. It was assumed that on this type of plot the tail from the peak at 226 mμ would be a straight line, and the most reasonable line was drawn. Subtraction of these values from those of the total spectrum gave a curve containing one or two maxima.

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[8] I. Nelidow and R. M. Diamond, *J. Phys. Chem.*, **59**, 710 (1955).

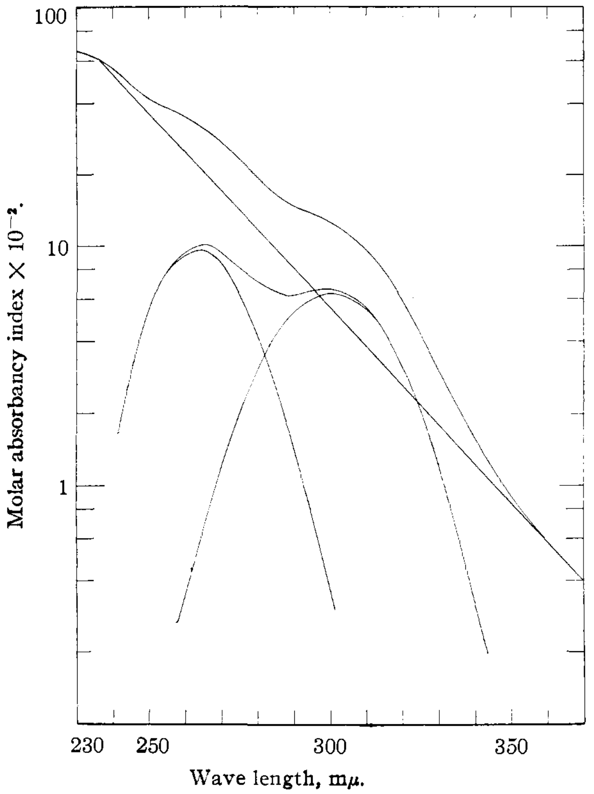

Fig. 3.—The spectrum of a solution 10.82 *M* in HCl, and the resolution of the spectrum into its component parts.

The absorption that causes the shoulder in the 260–270 mμ region resolved nicely by this method to give a maximum at 264 mμ (the species with two chlorines). In the solutions 10 *M* or greater in HCl a second maximum occurred at about 300 mμ. Since the resolved spectrum from the 6 *M* HCl solution was predominantly that of the two-chlorine species, it was used to further resolve the spectra in the higher acid concentrations. Figure 3 shows an example of how this leads to a resolved peak with a maximum at 302 mμ (the species with three chlorines). The height of each resolved peak then served as a measure of the amount of that component. The solutions 8–12 *M* in HCl display isosbestic points at 256 and 274 mμ, indicating the presence of only two species. This fact, in conjunction with the observed peak heights, allowed calculation of the peak heights for the pure components and the abundance of each component in the various solutions. Table I shows the abundances determined in this way.

It was possible to reconstruct the entire spectrum for each of these species in the following way. For a solution containing only two components, I and II, it is true that $A_{\text{obsd}} = A_{\text{I}}F_{\text{I}} + A_{\text{II}}F_{\text{II}}$, where A_{obsd} is the observed molar absorbancy index, A_{I} and A_{II} are the corresponding values for the pure components, and F_{I} and F_{II} are the fractional amounts of Mo(VI) present in the respective forms. Plotting A_{obsd} *vs.* F_{I} should then give a straight line which has A_{I} as an intercept when $F_{\text{I}} = 1$, and has A_{II} as an intercept when $F_{\text{I}} = 0$. The absorbancy data for the five solutions of greatest acidity were treated in this way, using values of *F* corresponding to the percentages of Table I. For the majority of wave lengths all five points fell on a line; at no wave length was more than one point badly off a line. This consistency lends additional support to the results listed in Table I. The values of the intercepts from these graphs gave the data necessary to reconstruct the spectra of the two components. These are shown in Fig. 1.

TABLE I

ABUNDANCES OF Mo(VI) SPECIES IN HYDROCHLORIC ACID

HCl, *M*	% present as 2-chlorine species	% present as 3-chlorine species
11.72	52	48
10.82	60	40
9.90	69	31
8.90	81	19
7.97	87	13
6.94	91	7
5.98	93	1
4.94	88	..
4.00	79	..
2.97	51	..
1.98	25	..
0.99	20	..

Conclusions

Figure 4 shows an interesting relationship between the abundance of the 2-chlorine species and the behavior of these solutions with respect to ether extraction and retention on an anion-exchange resin. The extraction work is that of Nelidow and Diamond[8] and the anion-exchange report that of

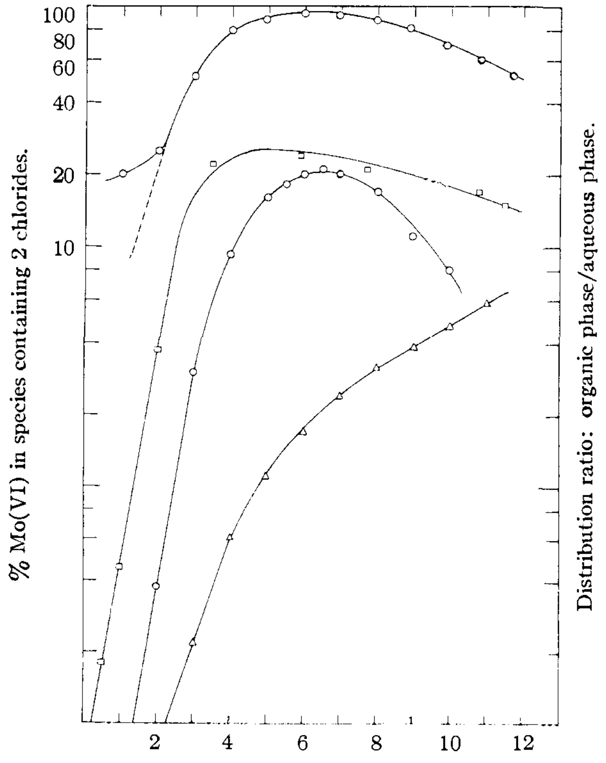

Fig. 4.—The abundance of the species containing two chlorines (upper curve, left hand ordinate), compared to distribution ratios for an anion-exchange resin[9] (□), isopropyl ether[8] (○), and dichloroethyl ether[8] (△).

Kraus, Nelson and Moore.[9] The values of the ordinates for the distribution data are purely relative for each of the functions plotted; the shapes of the curves are the feature of consequence. Although all the evidence relating to the extraction by ethers indicates that the extracted species contains two chlorines, the fact that the extraction curves do not correspond to the spectral data is not surprising; the distribution depends on many factors other than the equilibrium in the aqueous phase, and this equilibrium itself is shifted due to the presence of ether in the aqueous phase. For example, a decrease in the distribution ratio for isopropyl ether would be expected at the highest acidities even if there were no decrease in the amount of the extractable species in the aqueous phase.[10] The rapid rise of all curves for acidities up to 4 M indicates that the equilibrium in the aqueous phase is the most important factor in determining the distributions at these conditions.

The anion resin data corresponds sufficiently well with the spectral data to suggest that the species containing two chlorines is the form bound by the anion exchanger.

The most glaring failure of correspondence is the apparent leveling off in the amount of the two-chlorine species in 1–2 M HCl. The most likely explanation is that these solutions contain another species of Mo(VI) that also has an absorption maximum in the 260–270 mμ region, and that the amount of the two-chlorine species actually follows the dashed line indicated on the figure. Examination of the spectrum of Mo(VI) in $HClO_4$ solutions indicates that species with such absorption characteristics are present at such acidities.

The trends displayed in the spectra of these chloro complexes of Mo(VI) are consistent with the trends displayed by other elements. The resolved peaks with maxima at 264 and 302 mμ are those associated with the Mo–Cl bond, and the complex with the larger number of chlorines has the absorption at the longer wave length. It is also of interest that the absorptions at the maxima of the two resolved curves differ by only 3% (well within the errors inherent in the method). This relationship has been observed previously with the chlorocomplexes of Sb(V),[11] but there are not sufficient data from other elements to decide whether this is a general type of behavior.

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[9] K. A. Kraus, F. Nelson and G. E. Moore, THIS JOURNAL, **77**, 3972 (1955).

[10] D. E. Campbell, A. H. Laurene and H. M. Clark, *ibid.*, **74**, 6193 (1952).

[11] H. M. Neumann, *ibid.*, **76**, 2611 (1954).

EVANSTON, ILLINOIS

[CONTRIBUTION OF THE DEPARTMENT OF CHEMISTRY, CLARK UNIVERSITY]

Metal Chelate Compounds as Catalysts in the Hydrolysis of Isopropyl Methylphosphonofluoridate and Diisopropylphosphorofluoridate[1]

BY R. C. COURTNEY, R. L. GUSTAFSON, S. J. WESTERBACK, H. HYYTIAINEN, S. C. CHABEREK, JR., AND A. E. MARTELL

RECEIVED SEPTEMBER 7, 1956

The rates of hydrolysis of Sarin and DFP have been studied in the presence of a wide variety of metal chelate compounds as catalysts. The metal ion which yielded the largest number of catalytic metal chelates was found to be Cu(II), while a number of metal chelates of UO_2(VI), ZrO(IV), Th(IV) and MoO_2(VI) were also found to have considerable activity. Although the Cu(II) catalysts were apparently in a class by themselves, the following characteristics were found to be required in these hydrolytic catalysts: 1, incomplete coördination of the metal ion by the ligand; or 2, presence of oxy groups (or hydrated oxy groups) attached to the metal in certain cases where coördination was apparently complete. The wide variety of active metal complexes of Cu which were investigated made it possible to observe the following factors which favor maximum catalytic activity: 1, the presence of two aquo groups on the metal; 2, low stability of the metal chelate compound; and 3, the presence of maximum positive charge on the metal chelate. The importance of steric factors is indicated by the high activity of Cu(II) chelates of highly substituted diamines.

The purpose of this investigation was to study the catalytic effects of various metal chelate compounds in the hydrolysis of the cholinesterase inhibitors known as Sarin (isopropyl methylphosphonofluoridate $(C_3H_7O)(CH_3)POF$ and DFP (diisopropyl phosphorofluoridate, $(C_3H_7O)_2POF$). Wagner-Jauregg, *et al.*,[2] have recently reported that Cu(II) chelates active as catalysts in the hydrolysis of DFP contain a 1:1 molar ratio of the Cu(II) ion to a number of ligands, which include various α-amino acids and diamines. More recently Ryland, *et al.*,[3] have described a detailed study of the catalytic activity of the Cu(II) chelates of ethylenediamine, dipyridyl and *o*-phenanthroline, and have proposed a mechanism to explain the observed rates as a function of the metal chelate species present under their experimental conditions. The only other study of metal ion catalysis of hydrolysis of cholinesterase inhibitors is a report by Augustinsson and Heimbürger[4] which describes the effectiveness of Cu(II), Ni(II), Co(II), Ag(I), Au(III) and Pd(II) salts in accelerating the hydrolysis of Tabun (N,N-dimethyl - ethylphosphoroamidocyanidate). No previous reports on the catalysis of Sarin hydrolysis by metal chelate compounds have appeared in the literature.

Experimental

The liberation of acid during hydrolysis of Sarin was measured as a function of time with a Beckman automatic titrator, which was operated so as to automatically maintain the experimental solution at constant pH by addition of

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[1] This paper reports work done under contract with the Chemical Corps, U. S. Army, Washington 25, D. C.

[2] T. Wagner-Jauregg, B. E. Hackley, Jr., T. A. Lies, O. O. Owens and R. Proper, THIS JOURNAL, **77**, 922 (1955).

[3] L. B. Ryland, F. M. Fowkes and G. S. Ronay, Paper No. 108, Division of Physical and Inorganic Chemistry, 128th National Meeting of the American Chemical Society, Minneapolis, Minn., September 11–16, 1955.

[4] K. B. Augustinsson and G. Heimbürger, *Acta Chem. Scand.*, **9** 383 (1955).