[A Contribution from the Department of Chemistry, University of Wisconsin]

Color Phenomena Associated with Quinquevalent Molybdenum Solutions. II. The Effect of Various Electrolytes

By C. F. Hiskey* and V. W. Meloche

Introduction

In a previous paper[1] preliminary observations on color phenomena in quinquevalent molybdenum solutions were reported. In those studies it was shown that the color changes produced in aqueous solutions by the addition or removal of hydrochloric acid had no time lag and were perfectly reproducible. Detailed studies of the change of absorption spectra as a function of the acid concentration listed in Fig. 1 indicated that the color phenomena observed could be explained only by assuming a four color component mechanism. This four color component mechanism was a minimum hypothesis with the possibility of more components being involved not excluded. For the four component mechanism two limiting sets of equilibria were set up

$$\begin{tikzcd} W \arrow[r, leftrightarrow] & X \arrow[r, leftrightarrow] & Y \arrow[r, leftrightarrow] & X \end{tikzcd}$$

and

$$\begin{tikzcd} & X \arrow[dl, leftrightarrow] \arrow[dr, leftrightarrow] \arrow[dd, leftrightarrow] & \\ W \arrow[rr, leftrightarrow] \arrow[dr, leftrightarrow] & & Z \arrow[dl, leftrightarrow] \\ & Y & \end{tikzcd}$$

involving transitions from the W component with an assumed absorption maximum below 360 mμ to the component X with an observed maximum at about 460 mμ. This, in turn, as the hydrochloric acid concentration was raised successively changed to the Y and Z components with an observed maximum at 600 mμ and an assumed maximum above 800 mμ, respectively.

From the data obtained it was not possible to decide between a mechanism involving equilibrium between two components at one time, or between the more complicated mechanisms which could be assumed. The purpose of the present study was to investigate the initial stage of this process by following the concentration of the X component colorimetrically.

It will be recalled that cold dilute quinquevalent molybdenum solutions containing little hydrochloric acid are nearly colorless but that if the acid concentration is increased an intensification of the amber color is observed. Similarly, it can be demonstrated that the addition of alkali chlorides has the same effect. Some of the alkali halides, were investigated in order to determine their relative effect on the W⟷X transition. In addition preliminary studies of the effect of other acids, such as hydrobromic acid and sulfuric acid, were made.

Experimental

The procedures employed in these studies were essentially identical with those used in the previous work. Solutions were prepared of a definite acid strength or of a definite salt concentration by mixing appropriate amounts of concentrated salt solutions and water with a fixed amount of standard quinquevalent molybdenum solution. The quinquevalent molybdenum solution was prepared by reduction of the molybdate in the silver reductor. The master solution thus formed was 2 *M* with hydrochloric acid and 0.0248 *M* with molybdenum. A small portion of this solution was then properly diluted and compared against the solvent prepared in a similar manner but with the molybdenum excluded. Although quinquevalent molybdenum solutions are unstable, the rate of atmospheric oxidation was not appreciable at 20° for the range of acid concentrations and the time intervals used in these measurements. The salts used in these studies were c. p. analyzed and were not subjected to any further purification.

For each of the various sets of solutions an appropriate solvent was prepared and used in determining the relative absorption. This was necessary because the colorimeter was of the Evelyn type using cylindrical cuvettes. With cylindrical cuvettes, changes in the index of refraction of the solutions, caused by the addition of large amounts of electrolyte, would appreciably alter the focusing of the light on the photocell.

Therefore, each standard solvent prepared was checked against water to determine the degree of this effect and the appropriate correction resulting therefrom was introduced into the value recorded for the molybdenum solution at that electrolyte concentration.

In those experiments in which bromides or hydrobromic acid were used, the quinquevalent molybdenum solutions were prepared in the silver reductor as usual, except that hydrobromic acid was substituted for the hydrochloric acid.[2] Although such a reduction has not been studied previously to determine its quantitative aspects, it was felt that, because hydrobromic acid is a more vigorous reductant than hydrochloric acid and because silver bromide is less soluble than silver chloride, the molybdenum would be quantitatively reduced to the quinquevalent state. Although there is a good possibility that under the more vigorous reducing conditions obtained with hydrobromic acid in the silver reductor some of the molybdenum could be reduced to the tri-valent state, there

---

* Present address: Department of Chemistry, University of Tennessee, Knoxville.

(1) Hiskey and Meloche, This Journal, **62** 1565 (1940).

(2) Birnbaum and Walden, *ibid.*, **60**, 64 (1938).

was little reason to feel that this would interfere with our study. A previous study[3] had shown that without elaborate protection the tri-valent molybdenum is quite easily oxidized to the pentavalent state by atmospheric interaction. By comparison with standard quinquevalent molybdenum solutions prepared with hydrochloric acid in the low acid range it was observed that the master solutions prepared were identical in their color intensity with those prepared using the hydrobromic acid.

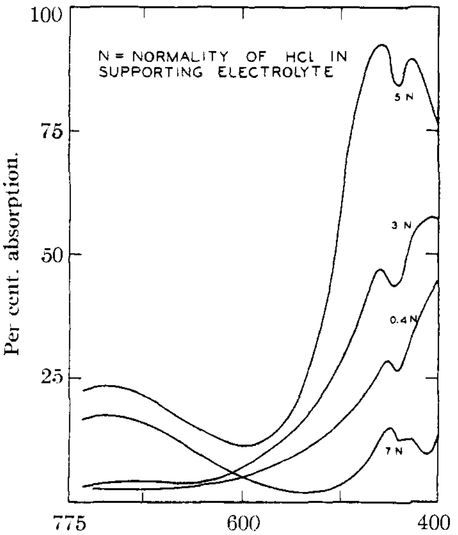

Fig. 1.

Results

In the first series of experiments a study of the relative effect of the concentration of chlorides of magnesium, hydrogen, lithium, sodium and potassium was made. The data obtained are plotted in Fig. 2 where 2 − log per cent. transmission[4] is given as a function of molarity of added electrolyte. All these measurements were made in the presence of 2 M hydrochloric acid because its presence was necessary in the preparation of the quinquevalent molybdenum. In order to relate the data on hydrochloric acid to those of the salts, it was necessary to shift that curve two moles to the left in the plot.

It is apparent from an examination of the plot that a very regular progression of effectiveness occurs as one goes through the series from potassium chloride to magnesium chloride. From the similarity of these curves it is obvious that the effect produced by the various electrolytes is qualitatively identical. Because of this fact it would seem likely that the effectiveness of these various salts can be related to each other by a simple constant. This expectation was checked by taking the concentration values from the plotted curves at different values of the color density. The concentration value of the hydrochloric acid was arbitrarily called unity and the other concentration values related to it. In Table I the data are considered in this way.

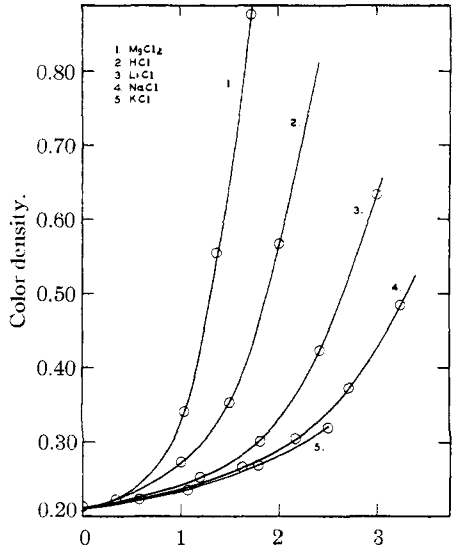

Fig. 2.—Effect of different electrolytes on the concentration of the "X" component (all in 2.0 molar HCl).

TABLE I

Salt added	Relative concentration needed to bring the color density to 0.30	0.35	0.40	0.45	0.50	0.55	Average ratio
$MgCl_2$	0.730	0.720	0.707	0.696	0.702	0.703	0.710
HCl	1.00	1.00	1.00	1.00	1.00	1.00	1.00
LiCl	1.46	1.42	1.41	1.40	1.40	1.41	1.42
NaCl	1.70	1.74	1.76	1.76	1.77	1.77	1.75
KCl	1.82	1.87	1.88	..	..	..	1.86

It will be observed that despite a wide range of color intensities the salt effect for the various ions is relatively constant. By simply multiplying the electrolyte concentrations by the average ratios listed for any given salt, all of the various points can be made to fall on the hydrochloric acid curve. Consequently, it should be possible to utilize these ratios in establishing relationships which might help to elucidate the mechanism of the process. It was observed that the ionic radii did not bear any qualitative relationship to the effects observed if the ionic radius of hydrogen

---

(3) Hiskey, Springer and Meloche, THIS JOURNAL, **61**, 3125 (1939).

(4) 2 − log per cent. transmission is used interchangeably in this paper with the expression color density. From the Lambert–Beer law expressed logarithmically

$$\log l/l_0 = -k'Cl = -kC$$

By rearrangement of the left-hand term

$$\log 100 - \log(100 \times l/l_0) = kC$$

2 − log per cent. transmission = kC = color density.

was kept in the series. There is, however, a qualitative relationship between the heat of hydration of the cations and the concentration ratio. By plotting the logarithm of the heats of ionic hydration[5] as a function of the logarithm of the salt ratios as listed in Table I, a straight line may be drawn through most of the points. This plot is given graphically in Fig. 3.

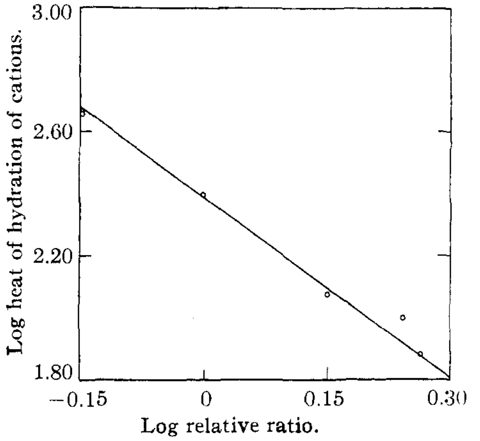

Fig. 3.—Log H = −0.193 log R.R. + 2.39.

Because of the presence of the high concentration of hydrochloric acid (2 *M*) in all of these experiments it was recognized that the ratios obtained could not be considered as being absolute, but it does seem reasonable to expect that if the hydrochloric acid has an effect on the ratios it would affect all of them uniformly. Thus the only result to be expected from changing the hydrochloric acid concentration would be to alter the slope of the curve in Fig. 3. To check the effect of the hydrochloric acid, an experiment was performed in which the concentration of the hydrochloric acid was reduced to 0.2 of a mole. In Fig. 4, the effectiveness of lithium chloride in such a hydrochloric acid solution is given. It is apparent that a change of the relative ratios exists. Studies along this line were unfortunately interrupted at this point and consequently no further consideration of this problem is possible at the present time. The determination of the absolute salt ratios by extrapolating the hydrochloric acid concentration to zero is contemplated. .

Next, it was decided to see what the effect of hydrobromic acid would be on the W⟵⟶X equilibrium. For that purpose the quinquevalent molybdenum solution was prepared in 2 *M* hydrobromic acid and the effect of magnesium bromide determined. In Fig. 5, a plot of the data obtained is given and for comparison the curve of magnesium chloride in 2 *M* hydrochloric acid is also given.

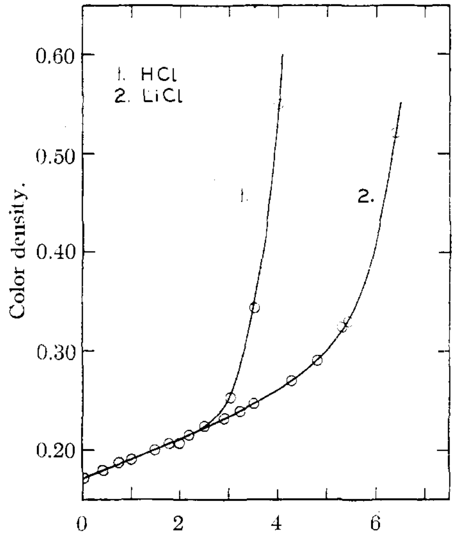

Fig. 4.—Effect of electrolyte concentration on concentration of "X" component (all in 0.2 molar HCl).

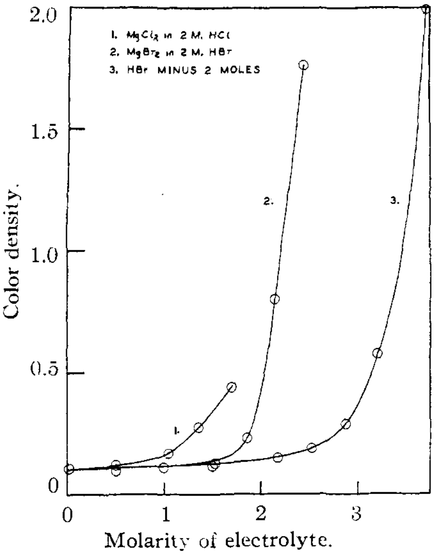

Fig. 5.

The effects observed are rather striking in that in the hydrobromic acid the threshold concentration of either the acid or salt required to initiate the transition is somewhat greater than that for the hydrochloric acid solutions, but once this threshold concentration is reached further addi-

---

(5) Latimer and Hildebrand, "Reference Book of Inorganic Chemistry," Macmillan Co., New York, N. Y., 1930, pp. 6, 28 and 46.

tion of small quantities of electrolyte produces remarkably striking shifts of the equilibrium in favor of the X component. Furthermore the color density in hydrochloric acid would not show a further rise on addition of more magnesium chloride but instead would show a break with the amber color component decreasing in concentration. For the solution given in Fig. 5, the maximum concentration of the X component that could be expected would correspond to a value of 0.5 for the term 2 − log per cent. transmission.

With the magnesium bromide it was not possible to add enough of the salt or of the acid to produce this break, but it is apparent that the concentration of the X component obtained was more than four times greater in the case of the hydrobromic acid than it was in the case of the magnesium chloride. It should also be emphasized that for any photo-electric colorimeter the error involved when the transmission approaches zero, is extremely high because the limit of the scale is reached. In this region it is possible for the color density to be doubled without observing any further change. Consequently, for any precise evaluation of these relative effects it would be necessary to work with more dilute solutions.

The interpretation of the results observed, as a result of a comparison with the effect produced by the various alkali halides in hydrochloric acid solution, seems to indicate that the effect of the hydrobromic acid differs in that once the threshold concentration is reached it shows a much greater ability to hold the equilibrium of the process in favor of the X component, whereas the hydrochloric acid system, while requiring less of a threshold concentration to initiate the W←→X transition, does not favor the X component to the same degree. With this detail in mind it seemed desirable to ascertain the effect of other substances on this equilibrium.

Of the various agents which might have been added sulfuric acid was chosen because of its dehydrating qualities and the color intensity curves as a function of sulfuric acid concentration were determined. Because of the important role which the hydrochloric acid concentration played in these determinations, the curves for the sulfuric acid were determined at six different hydrochloric acid concentrations ranging from 3.5 to 0.1 *M*. Furthermore, since these experiments were not limited by solubility difficulties as were those involving the salts, it was possible to carry the sulfuric acid concentrations to a sufficiently high level so as to observe the maxima of these curves and thus to observe the transition of the X component into the Y and Z components. These curves have been plotted in Fig. 6.

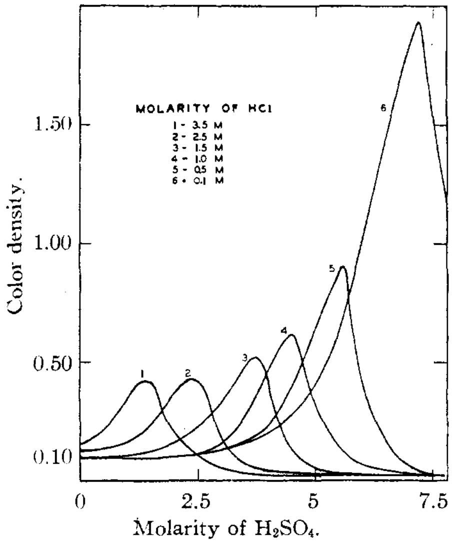

Fig. 6.

In all of the solutions a fixed amount of quinquevalent molybdenum was used. That two of the curves, namely, the 2.5 and the 3.5 *M* hydrochloric acid curves, do not intercept at the same point on the ordinate as do the rest of the curves, is explained by the effect of the hydrochloric acid concentration itself. As the hydrochloric acid concentration is reduced below 1.5 *N* the change in the intensity of color is undetectable and consequently all of the remaining curves originate at the same point.

This set of curves shows in a striking way what the effects of these two acids are. Again it is observed, just as in the case of the hydrobromic acid, that as the solution more and more takes on the character of a pure sulfuric acid solution the threshold value of sulfuric acid needed to initiate the transition rises; but at the same time, the equilibrium of the process is increasingly changed in favor of the X component with a consequent diminution in the concentration of the other forms. After the concentration of the X component has reached a maximum concentration characteristic for each set of hydrochloric and sulfuric acid concentrations further addition of sulfuric acid results in a displacement of the X component in favor of either the Y or Z components. As the sulfuric acid is steadily added the X component decreases in concentration in a manner which results in a curve symmetrical to the intensification curve with the color intensity decreasing to a constant minimum value for all of the curves for which data could be obtained.

Discussion of Results

While the information presented here does not permit of any complete statement concerning the character of the process as a whole, nevertheless, certain general conclusions may be drawn therefrom. For one thing, the effect of the halides has shown that in a general way the W←→X transition is related qualitatively to the hydrating power of the various ions used. The effects observed are in qualitative agreement with such properties as the solubility, heat of solution, the ability to form halides and the osmotic coefficient of the various halides studied. Fajans and Karagunis[6] have summarized these properties in a general table for all of the alkali halides and although in this study it has not been possible to present a thorough checking of the effectiveness of these various salts so that a complete comparison of this effect with their data can be made, it would seem that the evidence presented is sufficiently good to postulate an expected agreement. The complete verification, however, remains for future experimentation.

On the other hand, the evidence obtained in the sulfuric and hydrobromic acid solutions also suggests a hydration mechanism. On examination of the color intensity it seems necessary to recognize that at least two factors must be considered in the interpretation of the results. One of these is the role of the hydrogen ion concentration in the solution; the other is the tendency toward dipole–dipole interaction between the undissociated acids and the water in the system. At all concentrations in the process studied, both of these factors come into play, but the relative effectiveness of one or the other varies as the acid concentration varies.

In the lower acid concentrations where the hydrogen ion concentration is appreciable the shift of the W←→X equilibrium is related to the hydrating tendency of the cation. Thus it may be expected that the ability of the hydrogen ion to induce the W←→X transition will be similar to that of any other cation, but differing only in degree. This we have observed to be the case, for the alkali and alkaline earth halides studied where it was possible to set up relative ratios of effectiveness. While it is recognized that these ratios are not the true ratios because of having been determined in 2.0 N hydrochloric acid solutions, none the less, the qualitative outlines of the process are evident. That there should be a relationship between the heats of hydration of these ions and their relative effectiveness cannot be regarded as coincidental. On examination of curves in the sulfuric acid solution it is observed that as the concentration of the hydrochloric acid is lowered, a higher concentration of sulfuric is needed to bring the solution to the threshold of the color transition. Thus in 0.1 N hydrochloric acid, the sulfuric acid concentration needs to be raised to about 10.0 N before this threshold is reached, whereas, in the 3.5 N hydrochloric acid less than 1 M sulfuric acid is required. It is important to recognize that the total concentration of the acids required to induce the transition increases as the concentration of the hydrochloric acid is lowered indicating that the sulfuric acid is not furnishing hydrogen ions to the same degree that the hydrochloric acid is. This is in complete agreement with existing data. In terms of their ability to bring quinquevalent molybdenum to the threshold of its color transition, the sulfuric and the hydrochloric stand roughly in the same relationship to each other as their tendencies to furnish hydrogen ions to the system.

But, as was indicated above, the effectiveness of these acids in inducing the transition cannot be assumed to be wholly dependent on the hydrogen ion concentration which they furnish to the system. At least one other factor which must be considered is the relative ability of these substances to form hydrates. As a result of a dipole–dipole interaction, a certain amount of water in the system becomes attached to un-ionized hydrogen chloride and sulfuric acid. Consequently, their effect on the transition is altered when high concentrations are reached. For the hydrochloric acid the hydrogen ion concentration has been sufficient in the low concentrations to shift the transition equilibrium so far in favor of the X, Y and Z components that the dehydrating tendency of the hydrochloric acid, not particularly strong anyway, escapes detection. With the sulfuric acid we have a different situation. Here the hydrogen ion concentration is not sufficient to

---

(6) Fajans and Karagunis, *Z. angew. Chem.*, **43**, 1046 (1930).

shift the equilibrium to the Y and Z or even to the X forms before the dehydrating effect of the sulfuric acid, *per se*, comes into play.

Consequently, the effect on the relative concentrations of the various colored components will differ from that induced by the hydrogen ion alone. It is in this way that the extremely high concentrations of the X component, observed in Fig. 5, can be explained.

To recapitulate our argument in general terms, we may say that a substance not giving too high a hydrogen ion concentration when it, itself, is in relatively low concentrations, but possessing a tendency to dehydrate the system when it is taken in higher concentrations, will be effective in favoring high concentrations of X components. Such is the case of sulfuric acid, and such is the case for the hydrobromic acid systems.

In advancing an hydration mechanism it is important to emphasize that this need not necessarily be the sole process involved. Often, in equilibria of this sort autocomplex formation occurs. Usually such complex formation is indicated at least in this region of the periodic table by anomalous colors. Thus anhydrous cupric chloride is brownish-yellow, whereas in the hydrated state it has the characteristic blue-green color. Cobalt chloride shows an analogous color change.[7]

From the studies of quinquevalent molybdenum so far considered, it has not been possible to establish whether autocomplex formation analogous to the above is responsible for the phenomena observed. Additional studies involving measurements of ionic mobilities should help to solve this problem.

Acknowledgments.—The authors would like to express their appreciation to the Work Projects Administration for financial support for all of this work; to the Brittingham Foundation for the use of some of the spectrophotometric equipment and particularly to Mr. Max Wolf for his assistance in the experiments. Professors Norris F. Hall and Casimir Fajans were particularly helpful in their discussions of the problem.

Summary

A study of the transition of quinquevalent molybdenum from the colorless to the amber forms was made. The relative effect of a group of alkali chlorides in inducing the transition from the colorless to the amber form, was determined. The effect of hydrobromic acid and of magnesium bromide on the reaction was also measured. In addition the effect of sulfuric acid in various hydrochloric solutions was studied.

The data obtained were interpreted in terms of two factors which would have a dehydrating effect on the system under discussion. These factors were the hydrogen ion concentration and the tendency of an added solvent to unite with the water of the system by means of dipole–dipole interactions.

MADISON, WISCONSIN RECEIVED DECEMBER 16, 1940

---

(7) Howell, *et al.*, *Phil. Mag.*, **48**, 833 (1924); *J. Chem. Soc.*, 162 (1929); *Proc. Roy. Soc.* (London), **A142**, 587 (1936).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF NORTHWESTERN UNIVERSITY AND FROM THE RESEARCH LABORATORIES OF THE UNIVERSAL OIL PRODUCTS COMPANY]

The Catalytic Preparation and Interconversion of Simple and Mixed Ethers

BY V. N. IPATIEFF AND ROBERT L. BURWELL, JR.

It has been shown[1] that at high temperatures and pressures alumina serves as catalyst for the dehydration of methyl alcohol to form dimethyl ether. The behavior of alcohols and ethers in the presence of a "solid phosphoric acid" catalyst[2] was the subject of the present investigation.

The preparation of dimethyl ether represents a special case in the dehydration of alcohols in that an olefin cannot be formed. Continuous flow experiments at 350° and under 55 atmospheres pressure showed that solid phosphoric acid is an excellent catalyst for the production of dimethyl ether. It is durable and permits the use of very high space velocities.

At temperatures between 400 and 450° decomposition of dimethyl ether occurred.

The passage of an equimolar mixture of methanol and ethanol over the solid phosphoric acid catalyst at 336° under a pressure of 60 atm. pro-

---

(1) Ipatieff, *Ber.*, **37**, 2961 (1904).

(2) Ipatieff, "Catalytic Reactions at High Pressures and Temperatures," The Macmillan Company, New York, N. Y., 1936, p. 623.