Molybdenum(V) and Molybdenum(VI) Complexes with Gluconic Acid

BY J. T. SPENCE AND GEORGE KALLOS[1]

Mo(V) and Mo(VI) complexes with gluconic acid have been studied by polarography, coulometry, and polarimetry in the pH range from 2.0 to 7.0. The reduction of Mo(VI) to Mo(V) in the presence of gluconic acid is reversible, for a one-electron change, from pH 2.3 to 6.8. The diffusion current is linearly dependent on the molybdenum(VI) concentration at pH 2.3. Controlled potential coulometry indicates Mo(VI) is reduced to Mo(V) over the entire pH range while Mo(V) is reduced to Mo(IV) or Mo(III), depending on pH. The number of hydrogen ions involved in the electrode reaction and the molybdenum(VI)–gluconic acid ratio of the complex also are dependent on pH.

Many complexes of molybdenum with organic ligands have been reported but few have been investigated systematically. Furthermore, there is only a small number of complexes known which give reversible polarographic reduction waves.[2,3]

Gluconic acid forms complexes with many metal ions, including Ce(IV)[4] and U(VI).[5] Based on conductivity measurements, Richardson reported that Mo(VI) and gluconic acid form a complex,[6] but little data concerning this complex were given.

As part of a general study of molybdenum complexes, it seemed of interest to investigate the molybdenum–gluconic acid system, particularly with reference to its polarographic behavior. Accordingly, polarographic waves for Mo(VI)–gluconic acid complexes have been obtained over a wide pH range. In addition, coulometric and polarimetric data concerning these complexes are reported and the results discussed.

Experimental

Polarographic data were obtained with a Sargent Model XV recording polarograph using an H-type cell equipped with a saturated calomel reference electrode. The cell was immersed in a constant temperature bath maintained at 25.0 ± 0.1°. The precision of the half-wave potentials was found to be ±5 mv. The capillary had the following characteristics, measured at open circuit: m = 2.32 mg./sec., t = 2.60 sec./drop. All solutions were deaerated with purified nitrogen for 15 min. before polarograms were made. Diffusion currents were measured at the maximum of the oscillations. When the first wave was followed closely by the second wave, the diffusion current was measured at the inflection point. All currents were corrected for residual current.

Coulometric data were obtained using a specially constructed three-compartment cell, similar to that described by Meites,[7] with a mercury cathode and a platinum anode. Measurements were made by means of a gas coulometer in series with the cell. Provision was made for continuous bubbling of nitrogen during the course of reduction to prevent reoxidation of the lower oxidation states of molybdenum by atmospheric oxygen.

Polarimetric data were obtained with a Rudolph high precision polarimeter, equipped with an oscillating polarizer, photometer,

and monochromator, using a 100-watt zirconium concentrated arc light source. In order to obtain reasonable rotations, a wave length of 410 mμ was used at 2.00×10^{-2} M concentration and wave lengths of 320 and 350 mμ at 1.00×10^{-3} M concentrations. The precision of the data was ±0.005° of arc. All solutions were allowed to stand until equilibrium was reached.

Sodium molybdate (B. & A. Reagent) was dried for 24 hr. at 100° and analyzed by the α-benzoin oxime method[8] and found to contain 99.2 ± 0.3% Na$_2$MoO$_4$. Gluconic acid δ-lactone was purchased from Matheson, Coleman and Bell, and stock solutions were analyzed with standard NaOH. All materials used for buffers were reagent grade.

Results

Polarography.—Polarograms for the Mo(VI)–gluconic acid complex were obtained from pH 2.00 to 7.00. Representative waves are plotted in Fig. 1. From pH 2.0–3.0 two waves were obtained, the second approximately twice the height of the first. At pH 3.0 the second wave breaks into two waves of approximately equal height. Above pH 4.5 the second and third waves coalesce, giving two waves again. The reversibility of the waves was determined by plotting E vs. log $i/(i_d - i)$ and measuring the slope of the lines. The first wave was found to be reversible for a one-electron reduction from pH 2.3–6.8 at the concentration of gluconic acid indicated (a wave was considered reversible when the slope was within 10% of the theoretical value). In general, the other waves were irreversible.

The half-wave potential for the first wave was found to be independent of ligand concentration at any pH used.

The diffusion currents for the first and second waves at pH 2.3 were found to be proportional to the concentration of molybdenum(VI) over the concentration range used (Fig. 2).

$E_{1/2}$ was plotted vs. pH (Fig. 3) to determine the number of hydrogen ions involved in the electrode reaction. It can be seen that two lines were obtained and the slopes indicate 1.82 hydrogen ions per molybdenum from pH 2.3–5.0, and 0.88 hydrogen ions per molybdenum above this pH.

Coulometry.—In order to determine the number of electrons involved in each step of the reduction, con-

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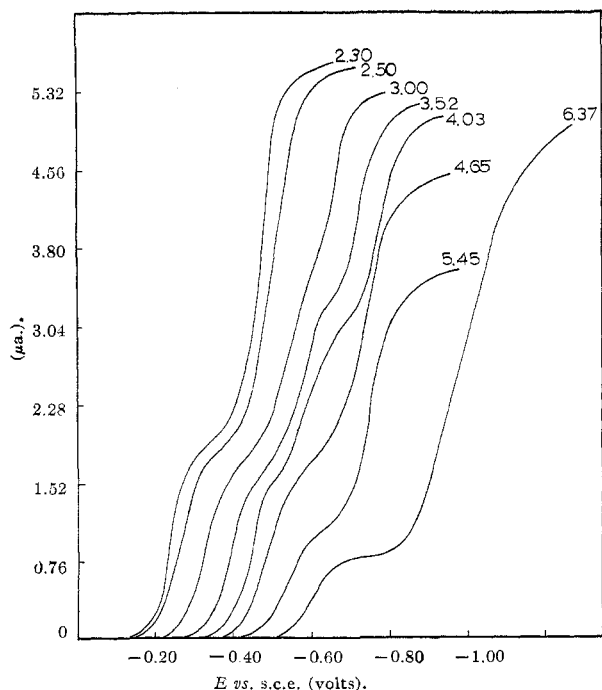(8) H. B. Knowles, *J. Res. Natl. Bur. Std.*, **9**, 1 (1932).

Fig. 1.—Polarographic reduction waves for Mo(VI)–gluconate complex at indicated pH values: [Mo(VI)] = 5.09 × 10⁻⁴ M; [gluconic acid] = 5.16 × 10⁻² M; [KCl] = 0.1 M; pH 2.50–4.00, no buffer; pH 4.00–5.50, acetate buffer; pH 5.50–6.80, phosphate buffer.

trolled potential coulometry at a mercury cathode was used. Table I gives the values of n (number of electrons/molybdenum) obtained at different pH and potential values.

At pH 2.50 the first wave is a one-electron reduction of Mo(VI) to Mo(V), and the second wave is a two-

TABLE I
COULOMETRIC DETERMINATION OF n

pH	E (volts $vs.$ s.c.e.)	n
2.50	−0.40	0.97
	− .70	2.87
4.00	− .52	1.00
	− .66	2.04
	− .85	2.95
5.40	− .71	1.00

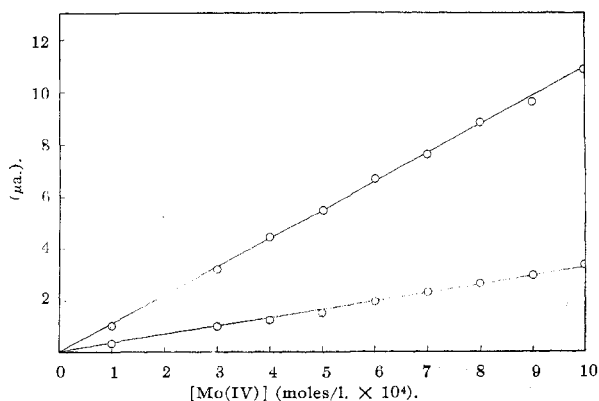Fig. 2.—Effect of [Mo(VI)] on diffusion current. Current in μa. is plotted $vs.$ [Mo(VI)]. Lower line, first wave; upper line, second wave; gluconic acid concentration = 0.1 M; pH 2.3.
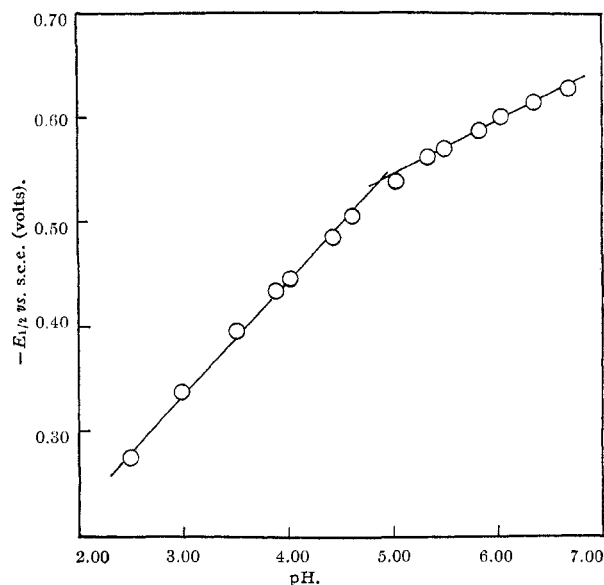

Fig. 3.—Effect of pH on $E_{1/2}$ for reduction of Mo(VI)–gluconate complex (first wave): [Mo(VI)] = 5.09 × 10⁻⁴ M; [gluconic acid] = 5.16 × 10⁻² M; [KCl] = 0.1 M; buffers used as in Fig. 1.

electron reduction of Mo(V) to Mo(III). At pH 4.00, both the second and third waves are one-electron reductions, most likely of Mo(V) to Mo(IV) and Mo(IV) to Mo(III), respectively.

Polarimetry.—When Mo(VI) is added to a solution of gluconic acid at a pH from 2–6 a large increase in optical rotation occurs, indicating complex formation. Figure 4 is a continuous variations plot of the difference in optical rotation between solutions containing Mo(VI) and gluconic acid and solutions containing the same concentration of gluconic acid $vs.$ mole fraction of Mo(VI) of the solutions at different pH and concentrations. The ratio of Mo(VI) to gluconic acid appears to be 2:1 at pH 2, but changes with increasing pH, approaching a 1:1 ratio. Figure 5 is a plot of pH $vs.$ optical rotation for the complex and indicates a maximum rotation at pH 3.9.

Discussion

Since the half-wave potential for the reduction of the Mo(VI)–gluconic acid complex is independent of ligand concentration, it is apparent that both Mo(V) and Mo(VI) form complexes containing the same number of ligands, at least under the polarographic conditions of a large excess of ligand. It is of interest to know whether the complexing species is gluconic acid or the gluconate ion. The pH of maximum optical rotation, which may indicate the pH of optimum complex formation, is 3.9. At this pH the ratio of gluconate ion to gluconic acid is approximately 2:1 (K_A for gluconic acid = 1.99 × 10⁻⁴).[9] At pH values below 2.5, where the ratio of salt to acid is 5 × 10⁻² or lower, the reduction wave becomes irreversible, at the concentration of gluconic acid indicated in Fig. 1, which may be expected when the ligand concentration be-

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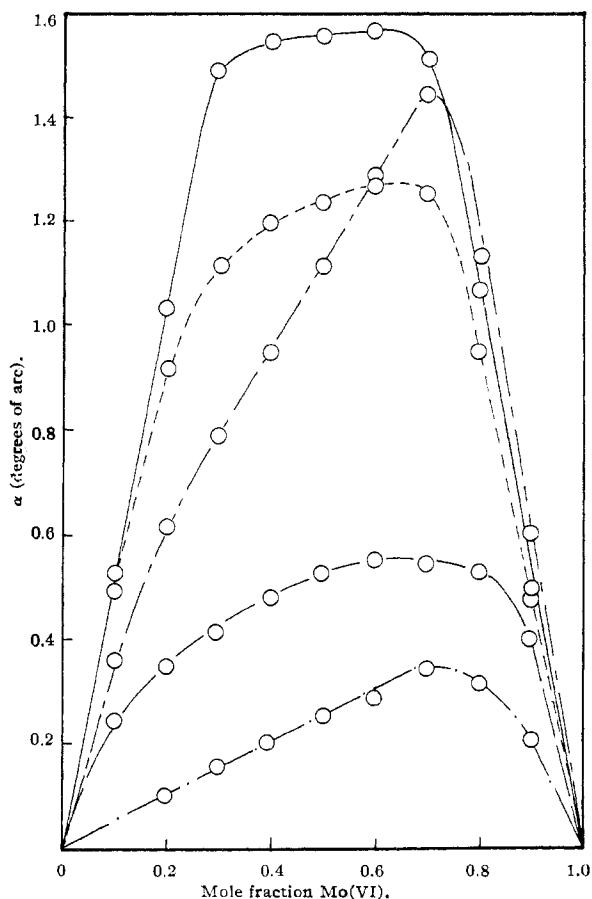
Fig. 4.—Continuous variations plot for Mo(VI)–gluconate complex. Difference in rotation between Mo(VI)–gluconic acid solutions and solutions containing the same amount of gluconic acid is plotted *vs.* mole fraction Mo(VI). — — —, pH 2.00; ————, pH 3.93; - - - -, pH 5.50, total concentration of Mo(VI) + gluconic acid = 2.00×10^{-2} M, λ = 410 mμ; — — —, pH 3.93, λ = 320 mμ; — — — —, pH 2.0, λ = 350 mμ, total concentration of Mo(VI) + gluconic acid = 1.00×10^{-3} M. pH 3.93, acetate buffer; pH 5.50, phosphate buffer.

comes small. In addition, when unbuffered solutions of Mo(VI) and gluconic acid at the same pH are mixed, the pH decreases. These observations indicate that the gluconate ion is most likely the complexing species.

There is some question concerning the molybdenum-(VI)–gluconic acid ratio of the complex. At pH 2.0, the continuous variations plots give sharp inflections at a molybdenum(VI):gluconic acid ratio of 2:1. Furthermore, the same sharp break in the curve and the same ratio were obtained at two rather different concentrations at this pH. It would appear that a 2:1 complex exists at low pH, while at higher pH a mixture of complexes is present, the change very likely being due to changes in the state of polymerization of molybdate with pH. Complexes in which the ratio of molybdenum(VI) to ligand is also 2:1 have been reported for flavin mononucleotide[10] and mannitol[11] at this same pH. It must be pointed out, however, that the method of continuous variations has certain limitations in a system such as this, and the results
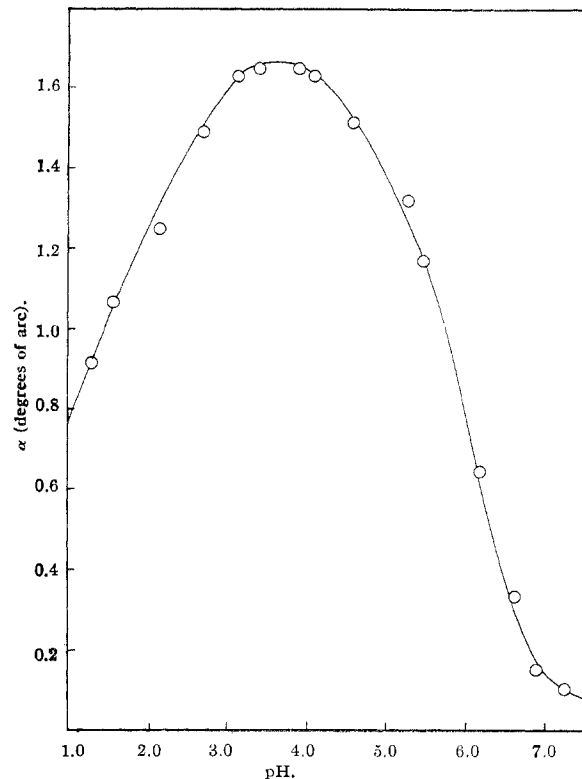

Fig. 5.— Effect of pH on optical rotation (α) of Mo(VI)–gluconate complex: [Mo(VI)] = 1.00×10^{-2} M; [gluconic acid] = 1.00×10^{-2} M; λ = 410 mμ.

must be interpreted with caution.[12] Under the polarographic conditions of a large excess of ligand the molybdenum(VI) to gluconic acid ratio probably approaches 1:1, particularly at higher pH. If this is the case, then the first reduction wave is reversible. Otherwise, if a 2:1 complex exists, it is irreversible since the reduction would involve two electrons per molecule. In view of this difficulty, and of the uncertainty involved in estimating the standard reduction potential for Mo(VI) at the pH of interest, no calculations of formation constants from the polarographic data were made.

A spectrophotometric study of the Mo(V)–gluconate complex was attempted. However, it was found that the absorbance of Mo(V) was not changed by the addition of gluconic acid. Furthermore, Mo(V) was oxidized almost as fast by atmospheric oxygen in the presence of gluconic acid as in its absence, indicating the Mo(V) complex is very weak.

It is apparent that the molybdenum(VI)–gluconate complex gives good polarographic reduction waves when the concentration of the gluconate ion is sufficiently great to complex all of the metal ion. It is of some interest that, in the pH range 3.0 to 4.0, molybdenum(VI) is reduced in three steps, first to Mo(V) and then to the very unstable Mo(IV) and finally to Mo(III), as is shown by the coulometric data. Apparently, in this pH range, the gluconate ion must form a complex with Mo(IV) which is sufficiently stable to permit its detection.

(10) J. T. Spence and J. Tocatlian, *J. Am. Chem. Soc.*, **83**, 816 (1961).
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The plot of pH *vs.* $E_{1/2}$ for the reduction of Mo(VI) to Mo(V) indicates two electrode reactions are involved, depending on pH. From pH 2.5 to 5.0 it is probable that two hydrogen ions are involved in the reduction (slope = 1.82) while from pH 5.0 to 7.0 only one hydrogen ion is involved (slope = 0.88). This difference undoubtedly reflects changes in the state of polymerization of molybdate with pH. A similar phenomenon was observed by Pecsok and Sawyer[3] with EDTA complexes of Mo(VI).

It is clear that under the proper conditions of pH and ligand concentration, gluconic acid will serve satisfactorily in the polarographic determination of Mo(VI). Furthermore, the data reported here indicate the possibility of the existence of other complexes with α-hydroxy acids, some of which may be of biochemical significance.

Structure and Nature of Bonding of $C_5H_5NiC_5H_5C_2(CO_2CH_3)_2$[1]

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The structure of $C_5H_5NiC_5H_5C_2(CO_2CH_3)_2$ has been determined from an X-ray analysis. The crystals contain four molecules in a monoclinic unit cell of symmetry Cc and dimensions a = 13.40 ± 0.02 Å., b = 13.78 ± 0.02 Å., c = 7.88 ± 0.01 Å., and β = 94°45′ ± 10′. Final least-squares refinement has yielded discrepancy factors of R_1 = 6.8% and R_2 = 7.5% for 978 observed reflections. The structure consists of discrete molecules in which a Ni(II) is covalently bonded to a π-cyclopentadienyl anion and a bicyclo[2.2.1]heptadienyl (*i.e.*, norbornadienyl) anion which coördinates to the metal *via* a σ-bond from the bridged carbon atom and a μ-bond from the olefinic group to which the methyl carboxylate substituents are attached. The $C_5H_5NiC_5H_5C_2$ fragment possesses an approximate mirror plane which passes through the nickel, one carbon of the cyclopentadienyl ring, and the bridge carbon and mid-points of the olefinic bonds of the norbornadienyl moiety. The Ni(II)–bridged carbon distance of 1.964 ± 0.012 Å. represents the first known value for a nickel bonded to a tetrahedral carbon atom. The unconjugated olefinic bond is symmetrically linked to the Ni(II) with an average Ni–C distance of 1.970 ± 0.009 Å.; the nickel distance to the mid-point of the olefinic bond is 1.83 Å. The olefinic C–C distance of 1.450 ± 0.016 Å. is significantly longer than the C–C distance of 1.330 ± 0.021 Å. for the uncoördinated olefin (of normal double bond length). A detailed comparison of the structural features of the norbornadienyl group in C_5H_5Ni-$C_5H_5C_2(CO_2CH_3)_2$ is made with those of the norbornadiene molecule itself and the molecule in chelated form as norbornadienedichloropalladium(II). Structural evidence for a small localized interaction between the Ni(II) and the cyclopentadienyl anion is given from the bond lengths and resulting molecular conformation. This specific interaction is ascribed to the perturbation of the π-electron density on the $C_5H_5^-$ anion by the ring's MO interaction with the dsp²-type hybrid orbitals of the Ni(II). The nature of this bonding is discussed with respect to recently found localized metal interactions with other π-organic systems.

Introduction

Alkyne complexes of binuclear cyclopentadienylnickel have been reported[3–5] in which an alkyne group as a distinct molecular entity utilizes its π-orbitals for bonding to each of the two nickel atoms by an electron-pair μ-type bond.[6] More recently a second type of cyclopentadienylnickel alkyne complex has been prepared by Dubeck[7] by the reaction of dicyclopentadienylnickel with dimethylacetylene dicarboxylate. Elemental analysis and molecular weight measurements suggested a mononuclear nickel complex formed by a bimolecular coupling of the two reactants. On the basis of the compound's diamagnetism, n.m.r. spectrum,

and degradative products, Dubeck[7] proposed a molecular model arising from the interaction of a nickel(II) with a π-cyclopentadienyl anion and with two electron-pair donors, one donor an aliphatic carbon (formerly a cyclopentadienyl carbon atom) and the other a non-conjugated olefinic group (formerly the alkyne).

The present X-ray study of $C_5H_5NiC_5H_5C_2(CO_2CH_3)_2$ has confirmed the over-all configuration of Dubeck's model. The molecular geometry provides evidence for a small localized interaction between the Ni(II) and the cyclopentadienyl anion. The nature of this bonding is described, and the criteria presumably necessary for the formation of similarly localized cyclopentadienyl-metal interactions are given. A detailed comparison of the molecular features of the compound with those of norbornadiene[8] and norbornadienedichloropalladium-(II)[9] is made.

(1) Presented in part at the 7th International Conference on Coördination Chemistry, Stockholm and Uppsala, Sweden, June, 1962.

(2) Based in part on a dissertation submitted by Chin Hsuan Wei to the Graduate School of the University of Wisconsin in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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