Kinetics and Complex Formation of Molybdate with Catechol[1]

Kenneth Kustin* and Sung-Tsuen Liu

Contribution from the Department of Chemistry, Brandeis University, Waltham, Massachusetts 02154. *Received October 26, 1972*

Abstract: A spectrophotometric determination of binding in molybdate–catechol (H_2L) solutions indicates the presence of two complexes. At 25° (±1), pH 7.3, and ionic strength 0.1 *M*, the stability constants for these two complexes are $K_1 = [MoO_2(OH)_2L^{2-}]/[MoO_4^{2-}][H_2L] = 37.1\ (\pm 5)\ M^{-1}$ and $K_2 = [MoO_2L_2^{2-}]/[MoO_2(OH)_2L^{2-}]\cdot[H_2L] = 1.52\ (\pm 0.4) \times 10^3\ M^{-1}$. Stopped-flow techniques were used to obtain the kinetic curves for the formation of these complexes; close-to-equilibrium relaxation theory was used for evaluation when consecutive reactions occurred. The apparent rate constants of formation and dissociation for each complex, under the same conditions given above are as follows: for the 1:1 (metal:ligand) complex, $k_1^{app} = (2.97 \pm 0.25) \times 10^2\ M^{-1}\ sec^{-1}$, $k_{-1}^{app} = 8.05 \pm 0.30\ sec^{-1}$; for the 1:2 complex, $k_2^{app} = (5.4 \pm 0.1) \times 10^2\ M^{-1}\ sec^{-1}$, $k_{-2}^{app} = 0.36 \pm 0.10\ sec^{-1}$. The reduced stability of the mono relative to the bis complex is due chiefly to the larger dissociation rate constant of the former. This effect is probably due to the presence of two inner-sphere hydroxide ions in the 1:1 complex, the π bonding of which to the molybdate center labilizes the bound catechol molecule.

It is now recognized that the molybdenum found in enzymes plays an important role in catalysis. As a result, interest in coordinated molybdenum has increased recently. However, very few studies are known in which both the binding and the kinetics of complex formation have been studied. An exception is the application of spectrophotometry and temperature jump to the examination of reactions of molybdate with 8-hydroxyquinoline.[2,3]

From earlier days it has been known that molybdate can react with catechol to form colored complexes.[4] This specific reaction has been developed for the quantitative analysis of molybdenum concentrations.[5] In neutral solution the orange-red color which is formed results from the presence of a 1:2 metal–ligand complex, while at pH's lower than 2 only a 1:1 complex is observed.[6]

An interesting feature of molybdate chelation is the greater stability of the 1:2 complex compared with the 1:1 complex. For example, although many investigations on the formation of complexes between molybdenum(VI) and catechol or catechol derivatives (usually by Job's method) have been carried out,[7-10] most of the results yield information relating only to the 1:2 complex. This effect is presumably due to the fact that the composition of the equilibrated molybdate–ligand solution is insensitive to changes in the relatively small concentration of mono complex. The phenomenon appears to be general, as a similar situation exists for other metal-containing oxyanions such as vanadate, stannate, and tungstate.[11]

In the present study, stability constants for both 1:1 and 1:2 molybdate–catechol complexes have been measured. Complexation has also been examined from a kinetic point of view to assist in distinguishing those steps in the mechanism which determine the predominance of a given complex.

Materials and Methods

Doubly distilled water was used throughout. Fisher reagent grade catechol, sodium molybdate, and other chemicals were used without further purification. Stock solutions of sodium molybdate were prepared by weight. To prevent oxidation by air, fresh solutions of catechol were prepared for each day's experiments by dissolving the required amounts of catechol in 0.01 *M* sodium bisulfite solution. Blank experiments with molybdate and bisulfite gave no indication of complex formation or other interaction.

All experiments were done at pH's above 7 in order to prevent any polymerization of molybdate which may occur in acidic solution.[12] The hydrogen ion concentration was kept constant by adding ammonium buffer solution; pH values were measured to ±0.01 pH unit with a Radiometer pH meter.

The temperature for this study was 25 ± 1°. The details of the stopped-flow apparatus have been described elsewhere.[13] Except in the measurement of the extinction coefficient of the 1:1 complex, the ionic strength, μ, was brought to 0.1 *M* with KNO_3. The optical spectra were measured with a Beckman DU spectrophotometer.

In stopped-flow experiments with molybdate in excess, two effects are observed. The shorter one ranges from 60 to 110 msec and corresponds to the formation of the 1:1 complex. The longer process lasts for a few seconds and is due to the consecutive formation of the second complex. Only the shorter effect was used to treat the first step of the reaction. In solutions with catechol in excess, only one effect is observed. It is due to a coupling of both reaction steps, and integration of the corresponding rate equation is therefore impractical. As a consequence, kinetic evaluation was achieved by employing relaxation theory for a system close to equilibrium (*vide infra*). Therefore only the last portion of each oscilloscopic trace was graphed. The "relaxation times" thus reported represent averages of at least three photographic determinations; relative error is within ±10%.

Results and Treatment of Data

Optical Spectra and Stability Constants. Spectra were taken from 300 to 540 nm (Figure 1). Catechol and molybdate do not show any significant absorption in this region. With catechol in excess, similar spectra are obtained as previously reported;[5,6] these absorption spectra have minima at 310 nm and maxima at 400 nm (Figure 1, curves A and B). These spectra result from the strong absorption of the 1:2 complex. As the catechol concentration is varied from 2.5 ×

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[1] The authors gratefully acknowledge support from the Public Health Service for Research Grant GM 08893-11, and from the National Science Foundation for Grant GB 33617.

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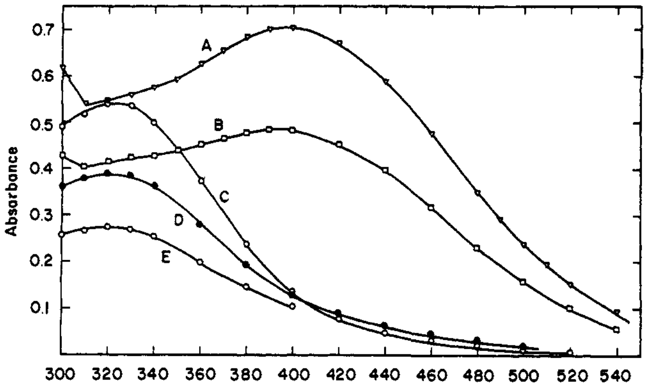


Figure 1. Absorption spectra of molybdate–catechol complexes, pH 7.3, temperature 25 ± 1°; (A) $[\text{catechol}]_0 = 7.5 \times 10^{-3}$, $[MoO_4^{2-}] = 2.0 \times 10^{-4}$ *M;* (B) $[\text{catechol}]_0 = 2.5 \times 10^{-3}$, $[MoO_4^{2-}] = 4.0 \times 10^{-4}$ *M;* (C) $[\text{catechol}]_0 = 2.0 \times 10^{-4}$, $[MoO_4^{2-}] = 2.0 \times 10^{-1}$ *M;* (D) $[\text{catechol}]_0 = 2.0 \times 10^{-4}$, $[MoO_4^{2-}] = 5.0 \times 10^{-2}$ *M;* (E) $[\text{catechol}]_0 = 2.0 \times 10^{-4}$, $[MoO_4^{2-}] = 2.0 \times 10^{-2}$ *M.* The maxium at about 325 nm is due to the 1:1 complex (C, D, E); the maxium at about 400 nm (A, B) is due to the 1:2 complex.

10^{-3} to 7.5×10^{-3} *M* and the molybdate concentration decreases below 4×10^{-4} *M*, Beer's law can only be followed at wavelengths higher than 440 nm, indicating that a 1:1 complex exists, the principal absorption of which lies below 400 nm.

To determine the stability constants for these complexes, the following procedures were adopted. At pH 7.3, with total catechol in large excess (total catechol was 1.5×10^{-1} *M* compared with a total molybdate of 1.0×10^{-4} *M*), the calculated molar absorptivities of the 1:2 complex are 5.03×10^3, 1.81×10^3, and 3.59×10^3 cm^{-1} M^{-1} at wavelengths 400, 500, and 330 nm, respectively. Due to the relatively low stability of the 1:1 complex, the molar absorptivity of this species is derived differently, namely, from a plot of 1/absorbance *vs.* 1/[total molybdate] with molybdate in excess. The extrapolated absorbance at infinite concentration of molybdate is used to calculate the absorptivity of the 1:1 complex. The value obtained is 3.03×10^3 cm^{-1} M^{-1} at 330 nm.

If MoO_4^{2-} is the free molybdate ion and H_2L is the neutral species of catechol, then the first two stepwise stability constants are (with K_1^{app} and K_2^{app} the apparent equilibrium quotients)

$$K_1^{\text{app}} \cong K_1 = [MoO_2(OH)_2L^{2-}]/[MoO_4^{2-}][H_2L]$$

$$K_2^{\text{app}} \cong K_2 = [MoO_2L_2^{2-}]/[MoO_2(OH)_2L^{2-}][H_2L]$$

These constants are found from an analysis of the excess molybdate spectra in the following way. Since the 1:1 complex does not absorb at wavelengths higher than 490 nm—Figure 1, curves C, D and E—the slight absorption at wavelengths higher than 490 nm in solutions of excess molybdate is due to the 1:2 complex. The concentration of this complex is calculated from the absorbance at one of the higher wavelengths, 500 nm for example. The total absorbance at one of the lower wavelengths, 330 nm in this case, is a sum of the absorbancies of both complexes; therefore, combining the measured total absorbance with a knowledge of the concentration of the 1:2 complex permits a determination of the concentration of the 1:1 complex. The stability constants are then calculated in a straightforward way from these concentrations and mass balance. The results of the stability constant measurements under varying conditions of concentration are given in Table I.

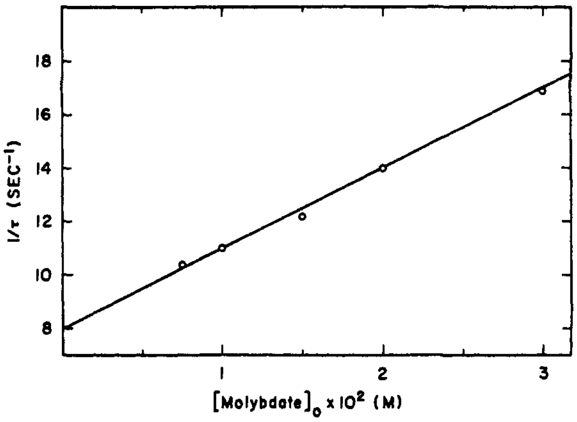


Figure 2. Plot of $1/\tau$ *vs.* $[MoO_4^{2-}]_0$. A calculated least-squares straight line has been drawn through the data points.

Table I. Stability Constants of Molybdate–Catechol Complexes[a]

$[\text{Molybdate}]_0$, *M*	$[\text{Catechol}]_0$, *M*	K_1, M^{-1} $\times 10^{-1}$	K_2, M^{-1} $\times 10^{-3}$	β_2, M^{-2} $\times 10^{-4}$
2.0×10^{-4}	2.5×10^{-3}			5.85
2.0×10^{-4}	5.0×10^{-3}			4.83
2.0×10^{-4}	7.5×10^{-3}			4.30
4.0×10^{-4}	5.0×10^{-3}			5.57
4.0×10^{-4}	2.5×10^{-3}			5.94
5.0×10^{-3}	2.0×10^{-4}	4.20	1.07	4.55
3.0×10^{-2}	4.0×10^{-4}	3.30	1.81	5.97
1.0×10^{-2}	4.0×10^{-4}	3.52	1.60	5.63
1.5×10^{-2}	4.0×10^{-4}	3.50	1.65	5.78
1.0×10^{-2}	2.0×10^{-4}	4.01	1.32	5.28
1.5×10^{-2}	2.0×10^{-4}	3.73	1.80	6.17
2.0×10^{-2}	2.0×10^{-4}	3.75	1.38	5.18

[a] At 25 ± 1°, pH 7.3, ionic strength 0.1 *M*. Average value of $K_1 = 37.1 \pm 5$ M^{-2}, $K_2 = (1.52 \pm 0.4) \times 10^3$ M^{-1}, and $\beta_2 = (5.42 \pm 1.0) \times 10^4$ M^{-2}. K_1 and K_2 are measured at 330 nm in excess molybdate solutions; $\beta_2 = K_1K_2$ is calculated at 500 nm in excess catechol solutions (β_2 values in molybdate excess solutions are calculated from the measured K_1 and K_2).

Rate Constants. At constant pH, and under pseudo-first-order conditions with molybdate in excess, the reciprocal of the observed relaxation time, τ, for the single-step formation of the 1:1 complex is

$$1/\tau = k_1^{\text{app}}[MoO_4^{2-}]_0 + k_{-1}^{\text{app}} \qquad (1)$$

where k_1^{app} and k_{-1}^{app} are the apparent association and dissociation rate constants and $[MoO_4^{2-}]_0$ is the total stoichiometric concentration of molybdate. A plot of τ^{-1} *vs.* $[MoO_4^{2-}]_0$ is linear as shown in Figure 2. A least-squares analysis has been carried out, with the aid of a PDP-10 computer, on the data shown in Figure 2 to determine the best values of the rate parameters in eq 1. The values thus obtained and the observed relaxation times are summarized in Table II. The ratio $k_1^{\text{app}}/k_{-1}^{\text{app}}$ is in good agreement with the spectrophotometric K_1 value (37 M^{-1}).

For reactions with catechol in excess, the close-to-equilibrium relaxation times for the consecutive reactions involve a second set of apparent rate constants,

Table II. Values of k_1^{app}, k_{-1}^{app}, and the Relaxation Time for the Formation of the 1:1 Complex[a]

[Molybdate]$_0$, $M \times 10^2$	pH	τ, msec
3.0	7.30	59.2
2.0	7.30	71.3
1.5	7.30	82.0
1.0	7.30	90.8
0.75	7.30	95.7
3.0	7.80	58.2
2.0	7.80	70.0
1.5	7.80	81.2
0.75	7.80	92.7
0.50	7.80	110.0

[a] At 25 ± 1°, [catechol]$_0$ = 5×10^{-5} M, ionic strength 0.1 M, $k_1^{\text{app}} = (2.93 \pm 0.2) \times 10^2$ and $(3.01 \pm 0.3) \times 10^2$ M^{-1} sec^{-1} at pH 7.3 and 7.8, respectively, and $k_{-1}^{\text{app}} = 8.1 \pm 0.2$ and 8.0 ± 0.4 sec^{-1} at pH 7.3 and 7.8, respectively.

k_2^{app} and k_{-2}^{app}, in addition to the first set. To find all four rate constants the general treatment for consecutive metal complex formation is applied to the complete reaction scheme described by the two constants, K_1 and K_2, yielding the following expression for the two relaxation times.[14]

$$1/\tau_{+,-} = {}^1/_2[(a_{11} + a_{22}) \pm \sqrt{(a_{11} + a_{22})^2 - 4(a_{11}a_{22} - a_{12}a_{21})}] \quad (2)$$

The a_{ij}'s are functions of the rate constants and concentrations of the species in solution. Since the concentration of catechol is large with respect to the other species in solution, the a_{ij}'s may be simplified according to the following.

$$a_{11} = k_1^{\text{app}}[\text{H}_2\text{L}] + k_{-1}^{\text{app}}$$

$$a_{12} = k_{-1}^{\text{app}}$$

$$a_{21} = k_2^{\text{app}}[\text{H}_2\text{L}]$$

$$a_{22} = k_2^{\text{app}}[\text{H}_2\text{L}] + k_{-2}^{\text{app}}$$

A trial and error program based on the above equations was then used to calculate the observed relaxation times. The rate constants producing the best agreement together with observed and calculated relaxation times are listed in Table III. All the observed relaxation times correspond to the negative root of eq 2. The differences between observed and calculated relaxation times are within ±15%. The values of the first set of apparent rate constants calculated in this way are in excellent agreement with those obtained from pseudo-first-order conditions where molybdate was in excess.

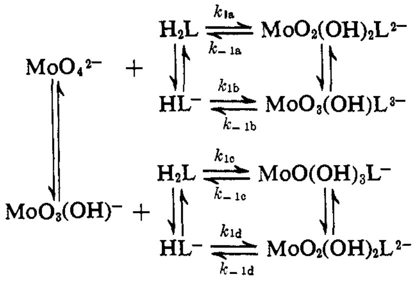
Table III. Rate Constants and Relaxation Times for the Two-Step Interaction between Molybdate and Catechol[a]

pH	[Catechol]$_0$, $M \times 10^2$	τ_{obsd}, sec	τ_{neg}, sec
7.3	1.50	0.475	0.462
7.3	1.00	0.765	0.772
7.3	0.80	1.00	1.01
7.3	0.70	1.12	1.16
7.3	0.60	1.36	1.36
7.3	0.30	2.45	2.25
7.6	1.25	0.68	0.59
7.6	1.00	0.88	0.78
7.6	0.90	0.92	0.88
7.0	1.50	0.46	0.46
7.0	1.00	0.68	0.77

[a] [Molybdate]$_0$ = 3×10^{-5} M, 25 ± 1°, ionic strength 0.1 M, $k_1^{\text{app}} = (2.9 \pm 0.3) \times 10^2$ M^{-1} sec^{-1}, $k_{-1}^{\text{app}} = 7.8$ sec^{-1}, $k_2^{\text{app}} = (5.4 \pm 0.1) \times 10^2$ M^{-1} sec^{-1}, $k_{-2}^{\text{app}} = 0.36$ sec^{-1}. Values of k_1^{app} and k_2^{app} are obtained from eq 2 when τ_{obsd} is in the best agreement with the calculated τ_{neg}. The reverse rate constants, k_{-1}^{app} and k_{-2}^{app}, are calculated from the equations $k_{-1}^{\text{app}} = k_1^{\text{app}}/K_1$ and $k_{-2}^{\text{app}} = k_2^{\text{app}}/K_2$.

Reaction Mechanism. The complete reaction scheme for the first step of complexation includes many pathways due to the existence of the various protonated forms of the reactants and products as shown in Scheme I. The relevant protolytic equilibrium constants are also shown. The completely deprotonated catechol species L^{2-} can be neglected under the conditions of this study. The protolytic reactions of catechol and molybdate are very rapid,[15] so that all vertical steps in Scheme I may be assumed to be equilibrated at all times compared with the (horizontal) complexation steps.

Scheme I



$$K_{\text{M}} = \frac{[\text{H}^+][\text{MoO}_4{}^{2-}]}{[\text{MoO}_3(\text{OH})^-]} \qquad K_{\text{ab}}{}^{\text{C}} = \frac{[\text{H}^+][\text{MoO}_3(\text{OH})\text{L}^{3-}]}{[\text{MoO}_2(\text{OH})_2\text{L}^{2-}]}$$

$$K_{\text{H}} = \frac{[\text{H}^+][\text{HL}^-]}{[\text{H}_2\text{L}]} \qquad K_{\text{cd}}{}^{\text{C}} = \frac{[\text{H}^+][\text{MoO}_2(\text{OH})_2\text{L}^{2-}]}{[\text{MoO(OH)}_3\text{L}^-]}$$

The experimental rate equation for formation of the 1:1 complex can be written

$$\text{d}[\text{C}]/\text{d}t = k_{1\text{f}}[\text{M}][\text{L}] - k_{1\text{r}}[\text{C}] \quad (3)$$

where

$$[\text{M}] = [\text{MoO}_4{}^{2-}] + [\text{MoO}_3(\text{OH})^-]$$

$$[\text{L}] = [\text{H}_2\text{L}] + [\text{HL}^-]$$

$$[\text{C}] = [\text{MoO(OH)}_3\text{L}^-] + [\text{MoO}_2(\text{OH})_2\text{L}^{2-}] + [\text{MoO}_3(\text{OH})\text{L}^{3-}]$$

and

$$k_{1\text{f}} = \frac{k_{1\text{a}} + \dfrac{k_{1\text{b}}K_{\text{H}}}{[\text{H}^+]} + \dfrac{k_{1\text{c}}[\text{H}^+]}{K_{\text{M}}} + k_{1\text{d}}\dfrac{K_{\text{H}}}{K_{\text{M}}}}{\left(1 + \dfrac{[\text{H}^+]}{K_{\text{M}}}\right)\left(1 + \dfrac{K_{\text{H}}}{[\text{H}^+]}\right)}$$

$$k_{1\text{r}} = \frac{k_{-1\text{a}} + k_{-1\text{b}}\dfrac{K_{\text{ab}}{}^{\text{C}}}{[\text{H}^+]} + k_{-1\text{c}}\dfrac{[\text{H}^+]}{K_{\text{cd}}{}^{\text{C}}} + k_{-1\text{d}}}{1 + \dfrac{[\text{H}^+]}{K_{\text{cd}}{}^{\text{C}}} + \dfrac{K_{\text{ab}}{}^{\text{C}}}{[\text{H}^+]}}$$

The relaxation time derived from eq 3 is

$$1/\tau = k_{1\text{f}}([\text{M}] + [\text{L}]) + k_{1\text{r}} \quad (4)$$

Since [M] ≫ [L], eq 3 is identical with the empirical equation (1), with $k_{1\text{f}} = k_1^{\text{app}}$ and $k_{1\text{r}} = k_{-1}^{\text{app}}$.

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It is possible to simplify the expressions for the rate constants. Since $[H^+] \sim 2\text{-}6 \times 10^{-8}$ *M* and $K_H = 2.9 \times 10^{-10}$ *M*,[16] then $[H^+] \gg K_H$ and

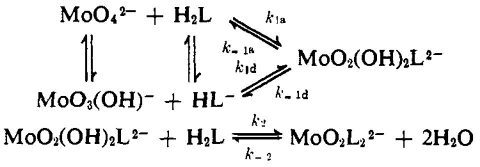
$$k_1^{app} \approx k_{1a} + k_{1d}(K_H/K_M) = 2.90 \times 10^2\ M^{-1}\ sec^{-1}$$

As shown in Table II, this approximation is justified, since k_1^{app} remains constant (within experimental error) as the pH changes from 7.3 to 7.8, indicating that the pathways corresponding to k_{1b} and k_{1c} contribute negligibly to the formation of the 1 : 1 complex. Therefore, $MoO_2(OH)_2L^{2-}$ is the only significant 1 : 1 complex.

For k_1^{app} two limiting cases can be distinguished: either $k_{1a} \gg k_{1d}K_H/K_M$ and $k_{1a} \approx 2.90 \times 10^2\ M^{-1}\ sec^{-1}$ or $k_{1d}K_H/K_M \gg k_{1a}$ in which case $k_{1d} \approx 1.9 \times 10^8\ M^{-1}\ sec^{-1}$, since $K_M \approx 1 \times 10^{-4}$.[2] The same arguments, when applied to the reverse rate constant, lead to the single complex $MoO_2(OH)_2L^{2-}$, whose overall dissociation rate constant is then $k_{-1}^{app} \approx k_{-1a} + k_{-1d} = 8.0\ sec^{-1}$.

As the pH changes from 7.0 to 7.6, the agreement between τ_{obsd} and τ_{calcd} in solutions where catechol is present in excess suggests that Scheme II represents the most probable reaction scheme during the kinetics of the consecutive reactions. This result shows that $k_2^{app} = k_2$ and $k_{-2}^{app} = k_{-2}$, within experimental error. Kinetically, it is not possible to distinguish pathway 1a from 1d. Therefore, k_{1f} and k_{1r} have been used to find the stepwise rate constants k_2 and k_{-2} given in Table III.

Scheme II



Discussion

The kinetic and spectrophotometric determinations with catechol clearly show that both 1 : 1 and 1 : 2 complexes are formed in mildly alkaline solution. This result is a departure from previous stability constant measurements,[5-8] in which only quantitative evidence of 1 : 2 complexes was found. The relatively larger stability constant of the higher order complex suggests that the greater proportion of the 1 : 2 complex simply masked the presence of the 1 : 1 complex. Before considering the reasons for this unusual ordering of stabilities, the catechol results will be compared with similar studies of molybdo-chelate stability and kinetics of formation.

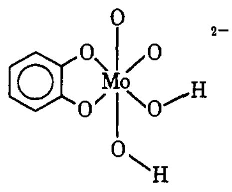
The stability constants of the catechol complexes indicate that the best conditions for the quantitative determination of molybdenum concentration in mildly alkaline solution are those which minimize interference by the 1 : 1 complex. Since our value for β_2 is essentially in agreement with those previously determined,[6,7] the additional precautions to observe are to use wavelengths higher than 460 nm and to keep catechol concentrations above 0.1 *M*.

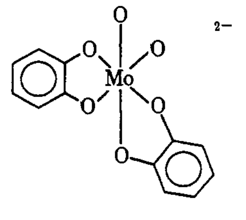
Kinetic studies of molybdate chelation are not numerous; despite some differences, however, the reactions of molybdate with 8-hydroxyquinoline (oxine) afford a convenient reference system.[2,3] Two species of complex with oxine (HOx) are formed during the first step of reaction, $MoO_3(OH)Ox^{2-}$ and $MoO_2(OH)_2Ox^-$. Neutral and anionic oxine are the attacking forms of the ligand; chelation is also evident in alkaline solution. In contrast, catechol forms only the $MoO_2(OH)_2L^{2-}$ complex and no chelation is evident in strongly alkaline solution. Apparently, only the partially and fully protonated catechol species are reactive. Nevertheless, the rate constants for the two systems are in remarkably close agreement. Thus, if we compare rate constants for reaction partners the sum of whose charges is −2, we have $k_{1a} = 2.90 \times 10^2\ M^{-1}\ sec^{-1}$ for H_2L compared with $4.1 \times 10^2\ M^{-1}\ sec^{-1}$ for HOx and $k_{1d} = 1.9 \times 10^8\ M^{-1}\ sec^{-1}$ for HL^- compared with $1.5 \times 10^8\ M^{-1}\ sec^{-1}$ for Ox^-. Differences in reactivity between protonated ligand species do not explain the difference in stability between the two complexes. Comparison of the rate constants determined in the catechol system suggests an explanation for the fact that $K_2 > K_1$; but, first, let us consider the nature of molybdate in solution.

In neutral and alkaline solution, the molybdate ion has a tetrahedral structure.[17] Adding ligands to molybdate changes the configuration around the metal ion from tetrahedral to octahedral. However, it has been postulated that $MoO_3(OH)^-$ already exists in solution in the form of an octahedral hydrate species.[18] Ultrasonic attenuation studies are in support of this conclusion,[15] as the rate constant for protonation of divalent molybdate was found to be less than diffusion controlled, although still representative of a rapid reaction. It therefore appears most likely that the process whereby coordination number expansion takes place is fast relative to complex formation and is not rate determining. Let us now consider the stability constants in light of the kinetic results.

In general, the stability constant for the second step of complex formation is usually less than that for the first step. As a first approximation, this effect is explained in terms of the statistical reduction in available sites for chelation and a decrease in electrostatic attraction. Since the charge product remains the same for both steps in catechol complex formation, only the statistical factor should play a role here. In the case of molybdo-catechol complex formation, K_2 is actually 41 times greater than K_1, and neither effect seems to prevail. This relation does not arise alone from differences in the forward rate constants, since k_2 is less than twice as large as k_1^{app}. The difference in stability is therefore primarily due to the difference in complex dissociation rate constant.

The overall dissociation constants of $k_{-1}^{app} = 8.0\ sec^{-1}$ and $k_{-2} = 0.36\ sec^{-1}$ chiefly account for the fact that $K_1 < K_2$. Let the two molybdo-catechol complexes be represented as shown.





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It can then be seen that the larger dissociation constant of the mono relative to the bis complex can be explained by the presence of the two hydroxy groups in the former and not in the latter compound.

Inner-sphere hydroxide ion is known to exert a strongly labilizing effect on other ligands coordinated to the central metal ion.[19] In some cases, the effect appears to be due to the replacement of a neutral ligand—water, for example—by one with a negative charge, which repels the other groups still attached to the metal ion in the inner coordination shell.[20] There should be little difference in this regard between dinegative catechol and two hydroxide ions; a more specific influence of hydroxide ion should be sought. This effect is most likely the donation of electron density from coordinated hydroxide ion to central molybdenum ion through ligand to metal π bonding.[21]

Catechol would not be expected to π bond to the metal as well as hydroxide, since the catechol oxygen p orbitals probably interact with those on the benzene ring and are "drawn" away from the metal. Therefore, the single catechol molecule in the mono complex is more strongly labilized by the two hydroxide ions, than are either of the two bound catechols in the bis complex by one of the remaining ones. It is also interesting to point out that in the oxine system, the species corresponding to the 1:1 complex, namely $MoO_2(OH)_2Ox^-$, which also possesses two OH^- groups, has a similar dissociation rate constant of 3.9 sec^{-1}.

The two forward rate constants, k_1^{app} and k_2, suggest further lines of investigation into the mechanism of molybdate complex formation. The reaction leading to formation of the mono complex may be regarded as an addition reaction.[22] In this case, expansion of coordination would have to occur,[23] and the two forward rate constants should be different, as formation of the bis complex presumably involves no further changes in coordination number. The two rate constants are quite similar, however. We feel this result suggests that chelation of molybdate is fundamentally a condensation or substitution reaction, one or more waters being eliminated upon substitution. More rate data on the coordination of this, and other, oxyanions should be collected before any conclusions are drawn on the nature of the complex formation steps.

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Microwave Spectrum, Structure, Dipole Moment, and Barrier to Internal Rotation of Phosphine–Borane

J. R. Durig,* Y. S. Li, L. A. Carreira, and J. D. Odom

Contribution from the Department of Chemistry, University of South Carolina, Columbia, South Carolina 29208. Received September 29, 1972

Abstract: The microwave spectra in the P, K, and R bands of 16 isotopic species of phosphine-borane (H_3PBH_3) have been measured and the following structural parameters have been determined: $d(BH) = 1.212 \pm 0.002$ Å, $d(PH) = 1.399 \pm 0.003$ Å, $d(PB) = 1.937 \pm 0.005$ Å, $\angle BPH = 116.9 \pm 0.2°$, $\angle PBH = 103.6 \pm 0.2°$, $\angle HBH = 114.6 \pm 0.2°$, $\angle HPH = 101.3 \pm 0.2°$. The molecule was found to be in the staggered conformation. The value of the dipole moment obtained from Stark splittings is 4.00 ± 0.03 D in the ground state and in the first excited state of the torsional mode. The barrier to internal rotation was determined from both the splitting and relative intensity methods to be 2.47 ± 0.05 kcal/mol. The structural parameters and barrier to internal rotation are compared to the corresponding values for similar molecules.

Phosphine–borane was first prepared in 1940 by Gamble and Gilmont by mixing diborane(6) and phosphine at low temperatures.[1] However, they postulated the structure $[PH_4]^+[H_3BPH_2BH_3^-]$ on the basis of chemical evidence, and it was not until 1961 that a crystallographic study showed unequivocally that the solid was the monomeric H_3PBH_3.[2] A later investigation by Parry and coworkers concluded that "diborane diphosphine" was the monomer H_3PBH_3 in the solid and liquid based on nmr, infrared, and Raman spectra.[3]

The nature and strength of the dative σ bond formed between boron and phosphorus in trivalent electron-accepting boranes and electron-donating trivalent phosphines have been a source of considerable controversy. There are currently two hypotheses which have been advanced to explain the nature of the boron–phosphorus coordinate bond and which have attempted to shed some light on the "base strength reversal" which is observed with these molecules.[4,5] In addition, several microwave studies have been reported in which the structures of F_3PBH_3,[6] HF_2BPH_3,[7] CH_3-

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