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Equilibrium Studies of Aqueous Polymolybdate Solutions in 1 M NaCl Medium at 25 °C

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The potentiometric data for acidified molybdenum(VI) solutions (1 M NaCl at 25 °C) of Aveston et al. and Cruywagen have been reevaluated. The results show that the reaction scheme recently proposed and tested by using Sasaki and Sillēn's data (3 M $NaClO_4$ at 25 °C) again gives a better description of the data than either of the two schemes proposed by Sasaki and Sillēn and by Aveston et al. Our scheme is based on theoretical investigations and is extended to include some other species that have been determined experimentally. A previously proposed relationship between the acidity constants of M(VI) polymetalate ions and the average number of terminal oxygen atoms available for each negative charge also applies for the protonated polymolybdate ions in this system. The following species, denoted by (p,q) according to the general formula $H_p(MoO_4)_q^{(2q-p)-}$, have been considered: (1,1), (2,1), (8,7), (9,7), (10,7), (11,7), (12,8), and (13,8). The species (14,12), (15,12), and (16,12) as well as (64,36) and (32,18), which play a role under the conditions of Sasaki and Sillēn's measurements, are of no significance under the conditions of the data now recalculated, first because of the narrower concentration and acidification range and second because of the weaker ionic medium used. A change in the ionic medium from 3 M $NaClO_4$ to 1 M NaCl has the same effect on the relative concentrations of the species as a fivefold decrease in the total molybdenum concentration. Because of this effect, the data of Cruywagen on the other hand represent a de facto lower concentration range and, thus, allow the tentative identification of small polyions such as (3,2), (4,3), and/or (5,4). The influence of the ionic medium on the equilibria is seen mainly as a concentration effect rather than the effect of counterion binding as described in the literature.

Introduction

A reaction scheme[1] for molybdenum(VI) equilibria in aqueous solution, based on theoretical investigations[2] and extended to include species indicated by experimental methods, has recently been tested by using the potentiometric data of Sasaki and Sillēn[3] for the ionic medium 3 M $NaClO_4$ at 25 °C. The species included on theoretical grounds were the polymolybdate ions $Mo_7O_{24}^{6-}$ (8,7) and $Mo_8O_{26}^{4-}$ (12,8) and their protonated forms $HMo_7O_{24}^{5-}$ (9,7), $H_2Mo_7O_{24}^{4-}$ (10,7), $H_3Mo_7O_{24}^{3-}$ (11,7), and $HMo_8O_{26}^{3-}$ (13,8); the numbers in parentheses refer to the values of p and q in the general formula $H_p(MoO_4)_q^{(2q-p)-}$. The following experimentally determined species have been considered: $[Mo_{36}O_{112}(H_2O)_{16}]^{8-}$ (64,36),[4,5] the protonated monomers $HMoO_4^-$ (1,1) and H_2MoO_4 (2,1)[6-8] (or their aquotized forms[9]), and the dimeric cation (5,2).[10] Also justified on experimental grounds is the (8,7) ion,[11-13] which has already been included for theoretical reasons. These species are described collectively as a "basic set". This model gives a description[1] of the potentiometric data of Sasaki and Sillēn[3] somewhat better than the scheme chosen by the authors themselves,[7a] namely (1,1), (2,1), (8,7), (9,7), (10,7), (11,7), (34,19), and (5,2). The basic set is also significantly better[1] than the scheme proposed by Aveston et al.,[11] namely (1,1), (2,1), (8,7), (9,7), (10,7), and (12,8).

Addition of another four species, namely (14,12), its protonated forms (15,12) and (16,12), and (32,18), led to a significant improvement of the basic model.[1] The choice was based on an analysis of the differences between observed and calculated (for the basic set) Z values and on some indirect experimental evidence.[14]

In this paper we report an analogous treatment and interpretation of two sets of potentiometric data (1 M NaCl medium at 25 °C) previously published in this journal by Aveston et al.[11] and Cruywagen.[15] A reevaluation of the data is important for several reasons: (1) For some other experimental investigations of the polymolybdate system, e.g. enthalpimetric and kinetic methods,[15-17] a knowledge of the species and their formation constants is essential. (2) The species (14,12), (15,12), and (16,12) have been postulated as a result of the reinterpretation of Sasaki and Sillēn's data.[1] It is therefore desirable to confirm their existence by using some other potentiometric data. (3) Finally, the possibility arose to investigate the effect of the ionic medium on the equilibria. According to the literature, the ionic medium has a pronounced effect, which stabilizes polyions[11,18] and may also influence the nature of the species that occur in solution.[17-20] However, according to our hypothesis[1,2] about possible species that could exist in aqueous solution, the nature of such species should be independent of the concentration and composition of the medium.

Treatment of the Data

The treatment of the data has been described elsewhere.[1] The value of the standard deviation σ_Z for a given set of species compared to the minimum standard deviation, which represents the random experimental

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Table I. Test of Reaction Schemes by means of the Equilibrium Data (Z, log c_{H^+}, $C_{MoO_4^{2-}}$) of Aveston et al. (Medium: 1 M NaCl, 25 °C)

	log $\beta_{p,q}$																	
scheme	(1,1)	(2,1)	(8,7)	(9,7)	(10,7)	(11,7)	(12,8)	(13,8)	(64,36)	(5,2)	(7,5)	(9,8)	(69,36)	(14,12)	(15,12)	(16,12)	(32,18)	σ_Z
C	3.55	7.22	52.81	57.40	60.97	63.03	71.19	73.07	346.53	elim[b]								0.0073
	8[a]	*11*	*67*	*60*	*57*	*28*	*29*	*26*	*42*	*0*								
E	3.60	7.26	52.42	57.41	60.75	elim	71.44	73.32	elim		41.51	59.73	353.81					0.0056
	9	*12*	*25*	*65*	*38*	*0*	*51*	*51*	*0*		*16*	*44*	*27*					
F*	3.55	7.21	52.81	57.39	60.97	63.10	71.23	72.99	346.39					$\underline{91.73}$[c]	$\underline{96.73}$	$\underline{101.03}$	$\underline{171.69}$	0.0074
	8	*11*	*65*	*55*	*57*	*32*	*30*	*20*	*27*					*2*	*4*	*6*	*17*	

[a] In italics: maximum species fraction (%) attained by the species at a data point to indicate its importance in the scheme. [b] elim: during optimization the value of the formation constant became ≤0; i.e., the species was eliminated. [c] The underlined log β values have been introduced in accordance with other experimental results[1] (see text).

Table II. Test of the Equilibrium Data (Z, log c_{H^+}, $C_{MoO_4^{2-}}$) of Aveston et al. for Depressions of σ_Z in Reaction Scheme C (Schemes $D_{p,q}$)

		maximum species fraction (%) at a data point										
depression	additional species	(p,q)	(1,1)	(2,1)	(8,7)	(9,7)	(10,7)	(11,7)	(12,8)	(13,8)	(64,36)	σ_Z
I	(9,8)	*50*	*9*	*12*	*19*	*67*	*47*	*0*	*52*	*41*	*41*	0.0060
	(10,9)	*30*										0.0062
	(11,10)	*24*										0.0063
II	(36,18)	*21*	*8*	*11*	*67*	*59*	*57*	*14*	*34*	*45*	*0*	0.0069
	(69,36)	*26*										0.0069
	(267,150)	*49*										0.0069
III	(7,5)	*21*	*7*	*11*	*69*	*59*	*39*	*20*	*42*	*28*	*43*	0.0069
	(6,4)	*25*										0.0071
	(8,6)	*17*										0.0071

errors, was used together with $\Delta Z,Z$ scatter diagrams as criteria to judge how well this set represents the experimental data.

Results of Calculations

In this study all the experimental points of the data sets of Aveston et al.[11] and Cruywagen[15] have been used in the computations. Aveston et al. used only those points for which $Z \leq 1.50$ and Cruywagen those for which $Z \leq 1.40$ to eliminate the possible contribution of small amounts of species that could not be considered in the reaction models tested. Because of the rather strong covariance of the formation constants, caused by large overlapping of the equilibria, their standard deviations have little meaning (see also ref 11) and are therefore not reported. Instead, to concisely indicate the significance of the various species in a reaction scheme, their maximum species fraction (percentage of molybdenum bound in the species) under the experimental conditions is stated.

Data of Aveston et Al. The measurements comprise 68 data points in the range $C_{MoO_4^{2-}} = 0.08$–0.0012 M for $Z \leq 1.67$.

The reaction scheme suggested by Sasaki and Sillēn[7a] resulted in a standard deviation $\sigma_Z = 0.0075$ (scheme A1). After substituting the (34,19) species by the experimentally determined (64,36) species, $\sigma_Z = 0.0073$ was obtained (scheme A). The reaction scheme preferred by Aveston et al.[11] and supplemented by species (64,36) gave $\sigma_Z = 0.0116$ (scheme B). It was necessary to add a species for which $Z^+ = (p/q) > 1.50$, since Aveston et al. had no need to consider such a species for data pertaining to $Z \leq 1.50$. Our basic set led to $\sigma_Z = 0.0073$ (scheme C, Table I). Scheme B indicated some conspicuous systematic deviations in the $\Delta Z,Z$ diagram, while the other schemes gave reasonably balanced $\Delta Z,Z$ diagrams.

Next, the effect on σ_Z of introducing into the basic set (scheme C) various single species, covering wide ranges of q and Z^+ values (schemes $D_{p,q}$), was investigated. This revealed three minima for σ_Z: a prominent one in the ranges $q = 5$ to > 100 and $Z^+ = 0.75$ to 1.18, with the lowest value ($\sigma_Z = 0.0060$) at species (9,8); a weak minimum in the ranges $q = 7$ to $\gg 100$ and $Z^+ = 1.75$ to >2, extending over nearly the whole range of q and Z^+ values and passing for example through a (36,18) and (267,150) species ($\sigma_Z = 0.0069$); and a weak minimum in the ranges $q = 2$ to 6 and $Z^+ = 1.33$ to 1.50, with the lowest value ($\sigma_Z = 0.0069$) at the (7,5) species. Table II lists some of the results of these calculations. The $\Delta Z,Z$ diagrams for the various models indicated improvements in accordance with the lowering of the standard deviations.

Simultaneous addition of the three species (9,8), (69,36), and (7,5) to the basic set, giving model E, resulted in the smallest possible value for σ_Z, namely 0.0056 (Table I). This standard deviation should be considered as the result of random experimental errors.[1] The corresponding $\Delta Z,Z$ diagram is very well balanced.

The results of one further scheme are discussed in the following section.

Data of Cruywagen. The data comprise 324 measurements in the range $C_{MoO_4^{2-}} = 0.1$–0.0005 M for $Z \leq 1.50$.

The reaction scheme proposed by Sasaki and Sillēn gave a standard deviation $\sigma_Z = 0.0067$ (scheme A) and that of Aveston et al. gave $\sigma_Z = 0.0068$ (scheme B1). Supplementing this scheme by the species (64,36) led to no improvement because of its negligible contribution (scheme B). Our basic set (scheme C, Table III) gave, with elimination of the (11,7) species, the standard deviation $\sigma_Z = 0.0062$ (0.0062_0). Inclusion of the (11,7) species with a formation constant corresponding to a previously determined pK_a value of 2.0 gave only a slightly higher value for σ_Z, namely 0.0062_2 (scheme C*). The reason for this is the strong covariance of the formation constants for the (13,8) and (11,7) species as well as their small species fractions; the optimum formation conditions for these species lie outside the range of the experimental conditions. The $\Delta Z,Z$ diagrams for schemes A and B (or B1) clearly indicated some systematic deviations.

To the basic set (scheme C*) were again added single species, over a wide range of q and Z^+ values (schemes $D_{p,q}$), and the effect on σ_Z was determined. Also in this case, three minima were indicated for σ_Z: a very weak minimum in the ranges $q = 8$ to >100 and $Z^+ = 1.00$ to 1.17, with the lowest value at the species (9,8) and (10,9) ($\sigma_Z = 0.0060$); another very weak minimum in the ranges $q = 9$ to ~ 40 and $Z^+ = 1.50$ to 1.59, with the lowest value at the species (15,10) ($\sigma_Z = 0.0060$); and a prominent one in the ranges $q = 2$ to 6, $Z^+ = 1.25$ to 1.50, with the smallest value for σ_Z at species (3,2) and (4,3) ($\sigma_Z = 0.0052$). Some of the results of these calculations are given in Table IV. Here also the $\Delta Z,Z$ diagrams for the different schemes show small improvements in accordance with the decrease in the value of the standard deviation.

When the species (10,9) or (9,8), (15,10), and (3,2) were added simultaneously to the basic set, it resulted in the smallest possible value for σ_Z, namely 0.0050 (scheme E, Table III). This standard deviation should be regarded as the result of random errors. The corresponding $\Delta Z,Z$ diagram is very well balanced.

The results of calculations for two further schemes are discussed in the following section.

Discussion

The Quality of the Basic Model. If one (for the moment) ignores the minima, then the basic set gives, in terms of the standard

Table III. Test of Reaction Schemes by means of the Equilibrium Data (Z, log c_{H^+}, $C_{MoO_4^{2-}}$) of Cruywagen (Medium: 1 M NaCl, 25 °C)

	log $\beta_{p,q}$																		
scheme	(1,1)	(2,1)	(8,7)	(9,7)	(10,7)	(11,7)	(12,8)	(13,8)	(64,36)	(5,2)	(3,2)	(10,9)	(15,10)	(3,2)	(4,3)	(14,12)	(15,12)	(16,12)	σ_Z
C	3.48 *12*[a]	7.29 *30*	52.79 *65*	57.50 *67*	60.86 *43*	elim[b] *0*	71.57 *54*	73.47 *19*	...	...									0.0062
C*	3.49 *12*	7.29 *30*	52.79 *65*	57.50 *67*	60.88 *45*	$\underline{62.86}$[c] *11*	71.49 *47*	73.29 *14*											0.0062
E	3.42 *10*	7.22 *25*	52.75 *57*	57.47 *68*	60.76 *38*	63.15 *20*	71.17 *21*	elim *0*			14.71 *15*	66.05 *10*	89.76 *37*						0.0050
F*	3.49 *12*	7.28 *29*	52.79 *63*	57.50 *64*	60.88 *44*	$\underline{62.86}$ *11*	71.50 *48*	73.30 *13*								$\underline{91.73}$ *2*	$\underline{96.73}$ *3*	$\underline{101.03}$ *6*	0.0063
G*	3.36 *9*	7.24 *26*	52.79 *64*	57.43 *62*	60.73 *35*	$\underline{62.73}$ *10*	71.55 *59*	73.13 *10*						14.33 *6*	22.27 *9*	$\underline{91.73}$ *2*	$\underline{96.73}$ *4*	$\underline{101.03}$ *7*	0.0051

[a] See footnote *a*, Table I. [b] See footnote *b*, Table I. [c] See footnote *c*, Table I.

deviation σ_Z and the distribution of ΔZ residuals as a function of Z, the best description for all three sets of potentiometric measurements (all data points), namely those of Sasaki and Sillén,[3] Aveston et al.,[11] and Cruywagen.[15] The fit of the scheme proposed by Sasaki and Sillén[7a] is only slightly less "good"; it fits so well because a species with $Z^+ \sim 1.78$ has been included as well as the (11,7) species, which is a good substitute for the (12,8) and (13,8) species in terms of both Z^+ and q values. The poorer fit of the scheme of Aveston et al.[11] is due to the absence of highly aggregated species with $Z^+ \sim 1.78$ as well as species for which $1.5 < Z^+ < 1.78$.

The importance of the covariance of the formation constants of species with $Z^+ \sim 1.5$ is best seen from scheme $D_{15,10}$ (Table IV), in which the (15,10) species attains a high species fraction at the expense of the (12,8) species with only a slightly lower standard deviation. This shows clearly that this method alone is insufficient to clarify the system in the corresponding acidification range.

Effect of the Ionic Medium. If Tables I and III are compared with Table I of ref 1, it is seen that (for the basic set) the maximum share of species (8,7) at the optimum data point is considerably smaller for the data of both Aveston et al. and Cruywagen (ionic medium 1 M NaCl, 25 °C) than for the data of Sasaki and Sillén (ionic medium 3 M $NaClO_4$, 25 °C). This is due not only to the smaller total molybdenum(VI) concentration (Aveston et al., 0.08 M; Cruywagen, 0.1 M; Sasaki and Sillén, 0.16 M) but more importantly to the smaller formation constants. The smaller formation constants are a direct consequence of the weaker ionic medium, an effect that has been mentioned in the literature by various authors.[2f,11,18a,21]

To obtain a better understanding of this effect, we have compared the distribution diagrams of the species (i.e. the species fractions as a function of pH and $C_{moO_4^{2-}}$) for model C (Aveston's data) and model C* (Cruywagen's data), respectively, with that of model C (Sasaki and Sillén's data).[1] From this it is clear that changing the medium from 1 M NaCl to 3 M $NaClO_4$ has about the same effect as a fivefold increase in total molybdenum concentration (compare Figure 1 with Figure 9 of ref 1). A simple explanation for the effect of an increase in the concentration of the ionic medium on the condensation equilibria is that the water activity is decreased. A lower water activity will benefit all condensation reactions, the extent of which will depend on the number of water molecules involved in the reaction. The activity coefficients of the various ionic species (included together with the water activity in the formation constants) are of course also affected by an increase in the concentration of the ionic medium. The total effect is similar to that of an increase in molybdenum concentration.

In the literature, the effect of the ionic medium on condensation equilibria is usually ascribed to complexation (counterion binding) between medium cations and highly charged polymetalate anions.[11,19]

Occurrence of Other Species. For the data of Sasaki and Sillén, extending over a wider concentration range ($C_{MoO_4^{2-}} = 0.16$ to 0.0003 M, $Z \leq 1.79$, 469 data points) than the data evaluated in this paper, a depression of σ_Z has been caused by introducing the species (14,12), (15,12), and (16,12) to the basic set.[1] A second minimum due to the species (32,18)[1] and a third due to the species (9,8) have been observed. The meaning of the first two minima has been discussed elsewhere.[1] In view of the pattern of the $\Delta Z,Z$ diagram, the third minimum could be explained in terms of a (very small) systematic error in the determination of the slope of the measuring electrode, thus simulating the presence of the (9,8) species.[22]

For Aveston's measurements pertaining to 1 M NaCl, the situation for the highest molybdenum concentration, 0.08 M, is comparable to that for the concentration 0.016 M at 3 M $NaClO_4$, as discussed above. For model C it requires consideration of

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Table IV. Test of the Equilibrium Data (Z, $\log c_{H^+}$, $C_{MoO_4^{2-}}$) of Cruywagen for Depressions of σ_Z in Reaction Scheme C* (Schemes $D_{p,q}$)

			maximum species fraction (%) at a data point								
depression	additional species	(p,q)	(1,1)	(2,1)	(8,7)	(9,7)	(10,7)	(11,7)	(12,8)	(13,8)	σ_Z
I	(9,8)	*20*	*12*	*30*	*45*	*69*	*39*	*0*	*59*	*17*	0.0060
	(10,9)	*25*									0.0060
	(11,10)	*11*									0.0060
II	(15,10)	*51*	*12*	*31*	*65*	*66*	*47*	*0*	*12*	*18*	0.0060
	(18,12)	*39*									0.0060
	(21,14)	*34*									0.0061
III	(3,2)	*16*	*10*	*24*	*66*	*68*	*34*	*8*	*61*	*11*	0.0052
	(4,3)	*12*									0.0052
	(8,6)	*28*									0.0052
	(5,4)	*10*									0.0056

Table V. Improvement of σ_Z by Small Species Introduced in Reaction Scheme C*

additional species[a]	improvement $\Delta\sigma_Z$	additional species[b]	improvement $\Delta\sigma_Z$
(3,2)	0.0010	(2,2)	0.0000
(4,3)	0.0010	(4,3)	0.0010
(5,4)	0.0006	(6,4)	0.0005

[a] Small species expected according to an addition mechanism. [b] Small species forming chains of MoO_4 tetrahedra by condensation reactions.

species (14,12), (15,12), and (16,12) as well as (32,18) with the formation constants listed in Table I for model F*. Here the value of σ_Z remains practically constant, and a maximum share of 2, 4, 6, and 17% is calculated for these species. Owing to this small share of the species (14,12), (15,12), and (16,12), one could not expect to prove their existence from the residual differences in Z. The (32,18) species affects only two experimental points. These species therefore do not explain the observed depressions of σ_Z. It is, however, desirable to find the reason for the prominent minimum at species (9,8), which replaces the species (8,7) to a great extent (see Table II). The other minima are too small. Most probably, the σ_Z minima are the result of small experimental errors. In view of the pattern of the ΔZ,Z diagram, the minimum caused by the species (9,8) may again be ascribed to a systematic error in the determination of the slope of the electrode, as has been indicated for the data of Sasaki and Sillén.[22] From a structural and theoretical point of view, the species (9,8) is an unlikely possibility[2c] and is also not compatible with either the data of Sasaki and Sillén[1] or those of Cruywagen (see below).

For the measurements of Cruywagen the same applies with respect to the species (14,12), (15,12), and (16,12), as is the case for the data of Aveston et al. These species, with formation constants listed in Table III for set F*, led to a value of 0.0063 for σ_Z. As far as the species (32,18) and (64,36) are concerned, no conclusions can be drawn since no measurements have been made in the region where they are supposed to occur. The very shallow minimum for σ_Z caused by species (15,10) can be explained in terms of random experimental errors. The other very shallow minimum for the species (9,8) or (10,9) may, in view of the pattern of the ΔZ,Z diagram, again be ascribed to a very small systematic error in the determination of the slope of the electrode.

The prominent minimum that is obtained by the small species (3,2), (4,3), (8,6), (7,5), (5,4), and some others ought to receive further attention. Previously when testing various models, Cruywagen[15] also observed a minimum for σ_Z due to species (3,2). The species (3,2), (4,3) and (5,4) (Table III, scheme G*; Table IV) occur only for molybdenum concentrations ≤0.003 M with a share >5%, which represents the observation limit. (The larger species cannot be considered here because their relatively high share is partly caused by covariance at the expense of the species (9,7) and (10,7).) This implies an upper concentration limit $C_{MoO_4^{2-}} \sim 0.0006$ M for the observation of these small species in an ionic medium of 3 M $NaClO_4$, which means that in the concentration range of the data of Sasaki and Sillén these species hardly occur. However, their existence seems plausible; they should occur, according to the law of mass action, at very low concentrations of both molybdenum(VI) and ionic medium (Figure 1). Small aggregates that could form according to an addition mechanism[2i] would be, in the pH range 4–2.5, the species (3,2), (4,3), and (5,4), which agree with the form of the third minimum (Table V). Polyions that build up through condensation of H_2O to chains of MoO_4 tetrahedra would be species (2,2), (4,3), and (6,4), but they do not agree so well with the third minimum.

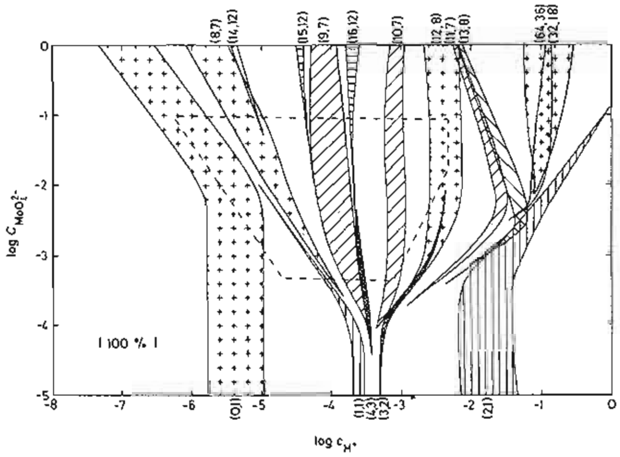

Figure 1. Existence area diagram for the various species of reaction scheme G* (data of Cruywagen; 1 M NaCl, 25 °C). The middle of each hatched area represents the conditions under which the various species attain their maximum concentration, while the width represents the fraction of molybdenum in the form of the species; the minimum species fraction indicated is 1%. For the (0,1) species, which occurs exclusively below a certain H^+ concentration, the H^+ concentrations chosen for the diagram correspond to a concentration of 99%. The broken lines confine the region in which the measurements of Cruywagen lie. For the sake of completeness, the reaction model has been extended to include the species (64,36) and (32,18) from the data of scheme F* (data of Aveston et al.).

Protonation Constants. Table VI shows that all three sets of data gave pK_a values of the correct order of magnitude and spacing (cf. ref 1) for the species (9,7), (10,7), (11,7), and (13,8) of the

Table VI. Acidity Constants of Protonated Polymolybdate Ions according to the Reaction Scheme Proposed by the Authors for Several Sets of Equilibrium Data in the Literature

		$-\log K_a$				
equilibrium data	reaction scheme	(9,7)	(10,7)	(11,7)	(13,8)	medium (25 °C)
Sasaki and Sillén	G*	4.38	3.38	1.87	1.83	3 M $Na(ClO_4)$
Aveston et al.	F*	4.58	3.58	2.13	1.76	1 M NaCl
Cruywagen	G*	4.64	3.30	2.00[a]	1.58	1 M NaCl

[a] This value has been introduced as obtained from other experimental results[1] (see text).

basic set modified by the species (14,12), (15,12), (16,12), (32,18), etc.; i.e., these values can be compared with the pK_a values of the mononuclear monobasic non-metal oxoacids in terms of the average number of terminal oxygen atoms available for each negative charge (cf. Figure 5, ref 1). The average positive deviation of ~1.4 pK_a units with respect to the non-metal oxoacids is attributed to the stronger p_π–d_π bonding between the transition-metal and oxygen atoms, as has been postulated previously to explain the weaker acidity of the mononuclear transition-metal oxoacids in comparison with the non-metal oxoacids.[23,24]

Existence Area Diagram. The existence area diagram (Figure 1) for the various species of scheme G* (data of Cruywagen) has been constructed to illustrate the effect of the ionic medium, 1 M NaCl in comparison with 3 M $NaClO_4$,[1] and also to give a vivid representation of the concentration ranges of the lower aggregated species.

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Registry No. Polymolybdate, 11116-47-5.

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(Dialkylamino)phosphines and Their Metal Carbonyl Complexes[1]

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Reductions with $LiAlH_4$ of (dialkylamino)dichlorophosphines, R_2NPCl_2, having sufficiently large dialkylamino groups lead to the corresponding (dialkylamino)phosphines, R_2NPH_2 (R_2N = dicyclohexylamino and 2,2,6,6-tetramethylpiperidino), as very air-sensitive liquids characterized by proton and phosphorus-31 NMR spectroscopy. These (dialkylamino)phosphines react with $(THF)M(CO)_n$ (M = Cr and W, $n = 5$; M = Fe, $n = 4$) to give the corresponding metal carbonyl complexes $R_2NPH_2M(CO)_n$. The complexes of the type $R_2NPH_2M(CO)_5$ (M = Cr and W) are yellow, sublimable solids, which are considerably more stable than the free R_2NPH_2 ligands. Reduction of (diisopropylamino)dichlorophosphine, $i\text{-}Pr_2NPCl_2$, with $LiAlH_4$ gives a solution shown by phosphorus-31 NMR to contain $i\text{-}Pr_2NPH_2$, but this product decomposes upon attempted isolation. However, the metal carbonyl complexes $i\text{-}Pr_2NPH_2M(CO)_5$ (M = Cr and W) can be isolated as relatively stable yellow sublimable solids by the $LiAlH_4$ reduction of the corresponding $i\text{-}Pr_2NPCl_2M(CO)_5$ complexes.

Introduction

During the past several years we have been interested in the synthesis and chemical reactivity of $(R_2N)_nPH_{3-n}$ derivatives. Previous papers from our laboratory[2–4] discuss bis(dialkylamino)phosphines, $(R_2N)_2PH$, a class of compounds that apparently was first prepared in the uncomplexed form by Soviet workers.[5,6] An important idea arising from our observations is the stabilization of uncomplexed $(R_2N)_2PH$ derivatives by the use of sufficiently bulky R_2N groups. Thus $(i\text{-}Pr_2N)_2PH$ is relatively stable and readily obtained by the $LiAlH_4$ reduction of $(i\text{-}Pr_2N)_2PCl$.[2–4] Analogous methods give $(Et_2N)_2PH$ in considerably lower yield but fail to give any detectable quantities of $(Me_2N)_2PH$.[4] O'Neal and Neilson[7] have also reported the P–H derivatives $(Me_3Si)_2NP(R)H$ (R = i-Pr, t-Bu, CH_2SiMe_3, $N(SiMe_3)_2$, and Ph) stabilized by the bulky bis(trimethylsilyl)amino group. These are prepared by reactions of the corresponding P–Cl derivatives $(Me_3Si)_2NP(R)Cl$ with $LiAlH_4$ or, less effectively, i-PrMgCl.

This paper describes attempts to apply similar ideas to the synthesis of stable R_2NPH_2 derivatives. Such derivatives are of interest since they can be regarded either as analogues of primary phosphines, RPH_2, or as dialkylamides of the unknown phosphinous acid, H_2POH, the phosphorus analogue of hydroxylamine. The only reported[8,9] examples of uncomplexed R_2NPH_2 derivatives appear to be the bis(trialkylsilyl)amino derivatives $(Me_3Si)_2NPH_2$ and $(t\text{-}BuMe_2Si)_2NPH_2$. In addition, a recent communication[10] describes the preparation of the tungsten pentacarbonyl complex $Et_2NPH_2W(CO)_5$.

Experimental Section

Microanalyses were performed by Atlantic Microanalytical Laboratory, Atlanta, GA. Proton NMR spectra (Table I) were taken on a Varian T-60 spectrometer. Carbon-13 and phosphorus-31 (Table I) NMR spectra were taken on a JEOL FX-90Q spectrometer operating in the Fourier-transform mode using proton noise decoupling in all of the carbon-13 spectra and in the phosphorus-31 spectra except when phosphorus–hydrogen coupling constants were being determined. Chemical shifts (δ) are reported in parts per million *down*field from internal tetramethylsilane (for proton and carbon-13 spectra) and external 85% phosphoric acid (for phosphorus-31 spectra).

All reactions were carried out in an efficient hood with aqueous calcium hypochlorite traps to decompose noxious materials in the effluent vapors before passing them into the hood exhaust. All air-sensitive organophosphorus and organometallic compounds were handled under nitrogen in Schlenk ware[11] or a polyethylene glovebag where necessary. All solvents were distilled under nitrogen over appropriate drying agents before use.

A recent paper from our laboratory[12] describes the preparations of the (dialkylamino)dichlorophosphine starting materials. Commercial Fe-

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