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^{95}Mo and ^{17}O NMR Studies of Aqueous Molybdate Solutions

Raisa I. Maksimovskaya* and Gennady M. Maksimov

Boreskov Institute of Catalysis, Lavrentiev pr. 5, Novosibirsk 630090, Russia

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Aqueous molybdate solutions with molybdenum concentrations of [Mo] = 1, 0.4, and 0.2 M have been studied by NMR at pH 7–1 and in 0.3–6 M $HClO_4$. The ^{95}Mo NMR spectrum of isopolyanion (IPA) $Mo_7O_{24}^{6-}$ (**I**) at pH = 5 consists of a signal at 210 ppm and two overlapping peaks at 32 and ~15 ppm with the intensity ratio ~1:4:2, and that of β-$Mo_8O_{26}^{4-}$ (**II**) consists of two signals at ~100 and 10 ppm with the intensity ratio ~1:3. A broad ^{95}Mo NMR line at around 0 ppm was observed in the pH range of IPA $Mo_{36}O_{112}^{8-}$ (**III**), and a signal of cationic oxospecies including MoO_2^{2+} (**IV**) was observed from –62 to –69 ppm. Two protonation sites of IPA **I** have been identified from ^{17}O NMR spectra, which suggests binding of up to two protons. The distribution diagram, derived from the ^{95}Mo NMR spectra, is given for [Mo] = 0.4 M. The ^{95}Mo NMR signals shift to lower frequencies with increasing number and strength of the Mo–O terminal bonds.

Introduction

Aqueous solutions of molybdenum(VI) are widely used in practical application including the syntheses of heteropoly acids and molybdenum-based catalysts. Molybdenum in its highest oxidation state of 6+ is always bound with electron-donating groups, considerably lowering its charge. Molybdenum combines most strongly with oxygen and fluorine. Trioxide MoO_3, a stable white crystalline powder with a greenish tint, behaves as an anhydride of the amphoteric molybdenum acid H_2MoO_4 that can dissociate in aqueous solutions by both acidic and basic mechanism.[1-3] In alkaline solutions there are monomeric MoO_4^{2-} anions forming salts with one to three valent cations, whereas in strongly acidic solutions (>6 N), the predominant form is a stable dioxocation MoO_2^{2+} ("molybdenyl"), which forms salts and complexes with inorganic or organic ligands.[4-9] The transformation of MoO_4^{2-} into cationic species occurs in several steps upon acidification via the action of protons forming H−O bonds comparable in strength to the Mo−O bonds.[2] Protonation begins in weakly acidic solutions and, at [Mo] $> 2 \times 10^{-4}$ M, protonated anions MoO_4^{2-} aggregate, with loss of some part of their oxygen, into the isopolyanions (IPAs).[11-13] The IPAs general formula is $[M_nO_{3n+a}]^{2a-}$ (where M = Mo or W and a = 1−6), and their formation can be described by the equation[13]

$$nMO_4^{2-} + 2(n-a)H^+ = [M_nO_{3n+a}]^{2a-} + (n-a)H_2O \quad (1)$$

The ratio of the stoichiometric coefficients in eq 1, $2(n - a)/n$, corresponds to the *degree of protonation,* $Z = p/q$, in the potentiometric measurements.[12] The solution composition, on the whole, depends on the *degree of acidification, P,* equal to the molar ratio of the added acid concentration to that of total molybdenum, $P = [H^+]/[Mo]$. An enormous amount of work has been carried out, and all possible analytical methods have been applied to characterize the IPA compositions in aqueous solutions.[12-15]

Precise potentiometric titration combined with mathematical analysis of the equilibrium curves is considered the best

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* To whom correspondence should be addressed. E-mail: rimax@catalysis.nsk.su. Fax: (+7)-383-330-95-73.

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method for determining the IPA compositions and equilibria.[10−15] However, experimental methods yielding a fingerprint of a species are necessary to check the proposed reaction models. In the last few decades, high-field NMR spectroscopy has been shown to be a very useful technique in studying polyoxomolybdates.[16−24] In 1979, the ^{17}O NMR spectra of CH_3CN solutions of tetrabutyl ammonium (TBA) salts of ^{17}O-enriched IPAs $Mo_2O_7^{2-}$, $Mo_6O_{19}^{2-}$, and α- and β-$Mo_8O_{26}^{4-}$ and aqueous solutions of $Na_6Mo_7O_{24}$ were reported.[16] The spectra were found to be unique for respective species and could be used for their identification in solutions. However, the low sensitivity of ^{17}O NMR complicated studies of aqueous solutions containing mixtures of several species. As suggested by the case of tungsten IPAs, the importance of the NMR measurements on the metal nuclei is evident.[18] The ^{183}W NMR spectra of tungsten IPAs are also structurally sensitive and contain fewer signals than the corresponding ^{17}O NMR spectra, for example, in the case of $W_7O_{24}^{6-}$, three and eight signals are found, respectively. Note that the ^{183}W and ^{17}O NMR spectra of IPAs complement each other similarly to ^{1}H and ^{13}C spectra in the NMR studies of organic compounds.

Compared with ^{183}W NMR, the ^{95}Mo NMR signals from Mo in its typical asymmetric environment are strongly broadened due to an appreciable electric quadrupole moment of the ^{95}Mo nucleus, which complicates spectral measurements and their interpretation for polymolybdates. The earlier measurements of the ^{95}Mo NMR spectra of IPAs $Mo_2O_7^{2-}$, $Mo_7O_{24}^{6-}$, $Mo_6O_{19}^{2-}$, and α- and β-$Mo_8O_{26}^{4-}$ have been done mainly in nonaqueous solutions and using ^{95}Mo enrichment (96%).[17,20] Subsequently, ^{95}Mo and ^{17}O NMR were applied to the study of aqueous solutions of Mo(VI).[18,19, 21−23] Only in two of these studies the NMR measurements were done in a different pH range, mainly on ^{95}Mo by Coddington and Taylor[22] and on ^{17}O by Howarth et al.[23] In the latter work the ^{17}O enrichment was used. On the basis of two ^{17}O NMR spectra (at pH 3.9 and 2.9) presented in the paper, the authors suggested the presence of a previously unknown IPA $H_3Mo_8O_{28}^{5-}$, intermediate between $Mo_7O_{24}^{6-}$ and β-$Mo_8O_{26}^{4-}$. At observation of the low-frequency shift of two ^{17}O NMR signals of $Mo_7O_{24}^{6-}$ upon acidification, the authors identified two protonation sites of the IPA.[23] At the same time, it was concluded that only monoprotonated $HMo_7O_{24}^{5-}$ is formed and that further protonation of heptamolybdate does not occur. This conclusion and the assumption of the $H_3Mo_8O_{28}^{5-}$ formation were used for further revision of the previously accepted hydrolytic reaction models.[25] However, both conclusions did not follow from the presented NMR data.[23] Our arguments on this issue are presented below in the discussion of the ^{17}O NMR spectra of $Mo_7O_{24}^{6-}$ and its protonation. It should be noted that the previous NMR measurements of molybdate solutions,[18,19,21−23] especially those on ^{95}Mo, were not sufficiently extensive. Howarth et al.[23] consider the ^{95}Mo spectra to be useful only as complementary information because of the isotope's large quadrupole moment and line broadening. In their paper they only present one ^{95}Mo NMR spectrum, measured at pH ∼3. In another study,[22] the ^{95}Mo spectra were measured in more detail at pH values of 6, 4.5, 3, and 1 and in a 6 M HNO_3 solution. In both papers, out of two signals observed at pH 3, the authors attribute to β-octamolybdate only the minor signal at 100 ppm, not taking into account that the analogous two peaks were observed in the spectrum of CH_3CN solution of TBA salt of β-octamolybdate.[17] Either, there is no conventional concept of the ^{95}Mo spectrum for heptamolybdate: two (220 and ∼30 ppm)[19,21] or one signal (∼30 ppm).[17,22,23,25] A single peak from the structures, containing three different types of Mo atoms, was explained by fast inter- and intramolecular exchange in aqueous molybdate solutions.[22] To the best of our knowledge, no other NMR studies of molybdate solutions have been published since 1990 and the above points have not been discussed elsewhere in more detail. We have been studying this system for about 10 years using in parallel ^{17}O and ^{95}Mo NMR at small pH changes, with different concentrations and methods of solution acidification, over a wide pH range. Such an approach, used before for studying Mo−V and W−V solutions,[19,26] can be described as "NMR titration". Because of the small changes of acidity, we were able to follow gradual changes of the spectra and better understand their origin. This work has two aspects, spectroscopic and analytical. For interpretation, the spectra of molybdenum IPAs were correlated with their structure and NMR data for similar IPAs of W^{VI} and V^{V}. We hope that our results will help in elucidation of the NMR spectra of isopolymolybdates and the acidity intervals of their stability.

Experimental Section

Concentrated sodium molybdate solutions (≥1 M), prepared from a $Na_2MoO_4 \cdot 2H_2O$ salt of reagent grade and distilled water, were decationized to different pH levels using the electrodialysis method. Acidification was carried out in the homemade two-chamber electrodialyzer previously described.[27] Platinized titanium and stainless steel (each of $S = 25$ cm^2) were used as the anode and cathode, respectively. The anodic and cathodic chambers (each of $V = 25$ cm^3) were separated by a cation-exchange membrane. The rate of flow in the chambers was 18 mL/min, and the current density was 0.1 A/cm^2. A solution of Na_2MoO_4 (1−1.5 M, 30 mL) was passed through the anodic chamber of electrodialyzer until the

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desired pH value was achieved. Simultaneously, an aqueous 0.1 M solution of NaOH was circulated through the cathodic chamber. Acidification with the use of electrodialysis provided minimum Na content and the absence of foreign anions in solutions, which allowed us largely to avoid the precipitation of molybdenum and to measure the ^{17}O NMR spectra at natural ^{17}O content. Thus, a 1 M solution of Na_2MoO_4, decationized to pH = 0.8 and with [Na] ~ 0.01 M, after being stored in a refrigerator for over 3 days, remained clear. For the preparation of strongly acidic solutions, concentrated $HClO_4$ was added up to 6 M concentration to the H_2MoO_4 solution prepared by electrodialysis. The 0.4 M molybdate solutions with different pH values were prepared from Na_2MoO_4 solution by acidification with dilute $HClO_4$. The degree of acidification, *P*, changed from 0.3 to 4 in small steps. Molybdate solutions in 2−6 M $HClO_4$ were prepared by the addition of concentrated $HClO_4$. Molybdate solutions of 0.03, 0.01, and 0.005 M concentration were prepared in 8, 8.2, and 8.4 M $HClO_4$, respectively. The 0.2 M molybdate solutions were prepared from the 0.4 M series by dilution.

The ^{17}O NMR spectra were measured on a Bruker MSL-400 NMR spectrometer using a high power probe head, at 54.24 MHz, with a 62.5 kHz sweep width, 10 μs pulse width, and 0.01 s interpulse delay, at natural ^{17}O content. The corresponding parameters for ^{95}Mo were 26.08 MHz, 20 kHz, 12 μs, and 0.2 and 1 s. The interpulse delay was chosen experimentally such that all signals did not saturate. It was equal to 0.2 s for polymolybdates, which is sufficient for the relaxation of molybdenum-95 nuclei in a distorted octahedral environment, and to 1 s for solutions containing tetrahedral MoO_4^{2-}. The NMR chemical shifts were determined relative to H_2O and 1 M Na_2MoO_4 external standards. For the evaluation of intensities of overlapping signals, the decomposition was made using the standard WIN NMR program. An average uncertainty in measuring intensities was about 20%.

Results and Discussion

^{17}O NMR Spectra. For the spectra of 1 M Na_2MoO_4, the solutions were measured in the pH range of 6−1 (Figure 1). A spectrum observed at a pH of 5.7 is well-known as the spectrum of $Mo_7O_{24}^{6-}$. The IPA contains MoO_6 polyhedra, **I**−**III**, and oxygen of eight types, for which the ^{17}O peak assignment was discussed elsewhere.[18] The signals of atoms $O_{F,G}$ and O_C bound with the Mo_{II} atoms (Figure 2a) are not visible at temperatures >13 °C because of the site exchange broadening caused by reorientation of the corresponding fragments within the IPA structure.[18,23] The rest of the peaks are also broadened and cannot be observed with an increase in temperature to 40−50 °C. For analogous IPA $W_7O_{24}^{6-}$, all types of O atoms are observed at 20 °C by noting the separate peaks becoming even sharper at 50 °C. These data show a higher lability of $Mo_7O_{24}^{6-}$. In this connection, the NMR measurements were mainly conducted at room temperature.

Beginning at a pH value of 5.5, heptamolybdate signals shifted with the increase in acidity. The δ ^{17}O−pH dependence indicates that the IPA is subject to protonation. In addition, a new set of signals appeared at around pH 4 and became clearly evident at pH <3 when the spectrum of heptamolybdate completely disappeared. This spectrum is practically identical to that measured in aqueous solution by Howarth et al.[23] in 1990 and is similar, except for the better resolution, to the spectrum of CH_3CN solution of β-$(Bu_4N)_3K[Mo_8O_{26}]\cdot 2H_2O$, published by Filowitz et al.[16] in 1979, which unambiguously confirms the existence of IPA β-$Mo_8O_{26}^{4-}$ in aqueous solutions. Unlike the previous study,[23] we have not used ^{17}O enrichment to avoid site selective oxygen exchange of IPA with ^{17}O enriched water, so the relative peak intensities in our spectra reflect the numbers of different O atoms in the structure. According to structural data,[28] the IPA contains oxygen of the following types (Figure 2b): 2 monooxo terminal (I), 12 *cis*-dioxo terminal (E-H), 6 doubly bridging (C and D), 4 3-fold bridging (B), and 2 5-fold

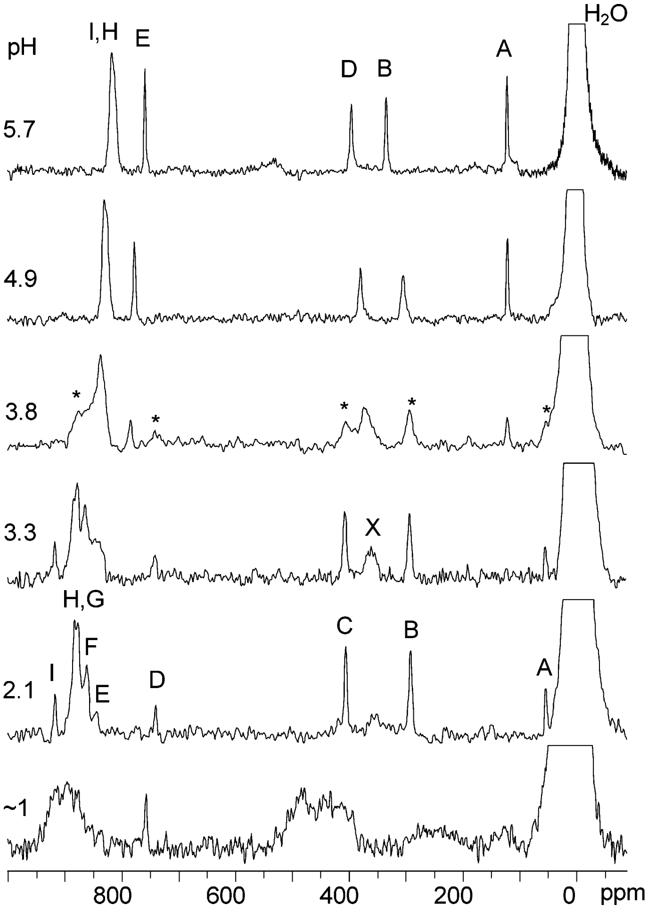

Figure 1. ^{17}O NMR spectra of Na_2MoO_4 solutions, [Mo] = 1 M, acidified by the electrodialysis method, at different pH; the number of pulses (np) equals (3−6) × 10^5, temperature (*T*) is 290−300 K; * indicates the β-$Mo_8O_{26}^{4-}$ peaks, and X is the unidentified signal. For the spectrum at pH ~1 [Mo] = 2 M, *T* = 300 K, np = 1.37 × 10^6. The peak labeling corresponds to Figure 2.

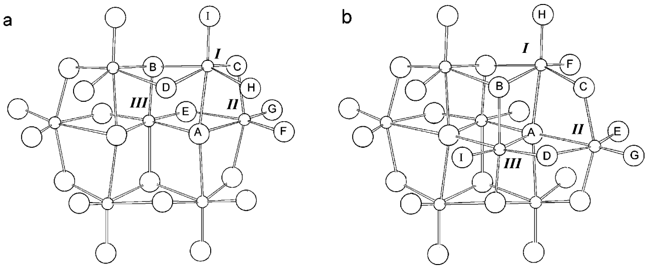

Figure 2. Idealized bond structures of the $Mo_7O_{24}^{6-}$ (a) and β-$Mo_8O_{26}^{4-}$ (b) IPAs.

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Table 1. ^{17}O and ^{95}Mo Chemical Shifts of Different Type O and Mo Atoms of Mo^{VI} Isopolyanions^{a}

Polyanion	δ ^{17}O (±1)			δ ^{95}Mo (±2)
$Mo_7O_{24}^{6-}$	O=Mo I, H G, F	Mo-O-Mo E D C	OM_3 OM_4, OM_5 B A	*I, II* *III*
pH 5.7	817 750	758 396 354	336 122	34 210
>5	815 745	754 395 356	339 122	27 - Ref.[23]
4.9	830	778 380	304 121	29 202
3.9	837	784 374	293 121	23 202
3.5				20 ~200
3.1				<20 ~200
β-$Mo_8O_{24}^{4-}$ pH 2.1	915(2) 876(2)* 882(4) 861(4) 844(2)	740(2) 406(4)	293(4) 54(2)	10 90
~3	917 878 876 861	738 404	291 56	100 Ref.[23]
* the number in parentheses indicates the approximate relative peak intensity				

^{a} Signal labeling corresponds to Figures 1 and 2.

bridging (A), all observed by the separate ^{17}O signals (Figure 1, pH 2.1). The signal assignments are based on the ^{17}O chemical shift scale for polymolybdates and the relative peak intensities.[29] Only the peak at δ ~360 ppm, observed at pH 2−3.5, does not relate to β-$Mo_8O_{26}^{4-}$. Clearly visible at 20 °C, it almost disappeared at 30−35 °C while the rest of the peaks narrowed with heating to ~50 °C. This peak may indicate the presence of α-$Mo_8O_{26}^{4-}$, whose signals, mainly coinciding by position with those of the β-isomer, strongly broaden at >4 °C because of the oxygen site exchange process within the IPA.[14−15,30,31] Note that the presence of the α-isomer in the CH_3CN solution of the β-isomer was also observed by a signal with a similar position in the ^{17}O NMR spectrum.[16,31] Failure to detect the α-isomer in aqueous solutions by the UV, IR, and Raman spectroscopy methods[14−15,31] does not exclude its presence as a minor species.

In the pH interval of ~4.5−3, where $Mo_7O_{24}^{6-}$ and β-$Mo_8O_{26}^{4-}$ coexist, their signals are noticeably broadened compared with their individual spectra (at pH values of 5.3 and 2.1, respectively) (Figure 1), which indicates the process of their chemical exchange, slow on the NMR time scale. Taking into account this broadening and the δ ^{17}O−pH dependence for heptamolybdate (Table 1), the spectra at pH values of 4.5−3 can be treated as the sum of the spectra of the above two IPAs without any intermediate species. A species postulated as $H_3Mo_8O_{28}^{5-}$ was proposed by Howarth et al.[23] with the ^{17}O NMR signal assignments at 261, 370, 395, 840, 850, and 860 ppm. However, the above signals coincide, within precision of δ-measurements, with the signals of heptamolybdate at the given pH and octamolybdate, except for the signal at 261 ppm. Interestingly, we have never observed the latter peak in our spectra. It could arise from the $HClO_4$ impurity ($\delta \approx 290$ ppm) or be a spectrometer artifact from the high ^{17}O sample enrichment. The rest of our spectrum at pH 3.8 (Figure 1) is close to the spectrum observed by Howarth et al. at pH 3.9, and it only represents a superposition of the broadened signals of hepta- and octamolybdates.

At pH values of ~1, we observe in the spectrum two groups of comparable intensity with overlapping broadened lines in the regions of 800−950 ppm and 400−500 ppm from Mo═O and Mo—O—Mo bonds, respectively. This spectrum does not contain much structural information except that it indicates the complex has large dimensions. According to published data, the predominant IPA at pH ~1 is $Mo_{36}O_{112}(H_2O)_{16}^{8-}$.[12,14−15] Note that the H_2O line is also broadened and shifted (~3−5 ppm) relative to heptamolybdate solutions, which is caused by the protonation of water molecules and their participation in exchange with the molybdate species.

Signal Shifts and Protonation. When an IPA is protonated, the protons attach to the most basic oxygens. The protonation sites can be identified from the low-frequency shift of the ^{17}O NMR signals.[32−34] In the ~5.5−3.9 pH interval, the peaks of O_B and O_D atoms of $Mo_7O_{24}^{6-}$ shift by about −40 and −25 ppm, respectively, which indicates that both of these sites are protonated (Table 1, Figure 1). These peaks evidently further shift upon acidification to pH values of 3.3−3.1, but we could not track them because of the decrease in the $Mo_7O_{24}^{6-}$ spectrum intensity. Similar ^{17}O shifts are shown on the δ ^{17}O−pH dependence for heptamolybdate reported by Howarth et al. (Figure 1, ref 23),

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although in their discussion the authors indicate that the protonation shift is only 20 ppm. On the basis of this value and the absence of clear inflections on the plot of the δ ^{17}O−pH dependence, which was expected between successive protonation steps of an IPA,[33] they suggest that $Mo_7O_{24}^{6-}$ undergoes only a single protonation. Accepting that two different sites, O_b (═O_B) and $O_{b'}$ (═O_D), are actually protonated, they suppose that protons bridge these O atoms in $HMo_7O_{24}^{6-}$ or protonate each site in turn. In our opinion, two different protonation sites favor $[H_2Mo_7O_{24}]^{4-}$. The main objections of Howarth et al.[23] against this form are small δ ^{17}O changes of protonated O atoms for heptamolybdate compared with $V_{10}O_{28}^{6-}$. It is known that δ ^{17}O changes upon acidification are caused by the lengthening of a M−O(H) bond. Because δ ^{17}O is less for O atoms bound with Mo than for similar O atoms bound with V,[16] the δ ^{17}O changes dependent on the bond length need not be equal; on the contrary, they are expected to be less for O−Mo bonds. In addition, there may be some other factors which influence the bond lengths in polyanions such as their geometry, dimension, interaction with counterions, etc. By the way, the δ ^{17}O changes upon acidification for $Mo_7O_{24}^{6-}$ are not too small as follows from Howarth et al.[23] and our data. They are comparable with the $H_2V_{10}O_{28}^{4-}$ changes of δ, reported by Harrison et al.,[33] which on the whole suggests that the second step of protonation of heptamolybdate is quite acceptable.

For β-$[Mo_8O_{26}]^{4-}$, the δ ^{17}O−pH dependence is not observed, which indicates that this IPA is resistant to protonation at least down to a pH value of ∼2.

^{95}Mo NMR Spectra. The spectra of the acidified 1, 0.4, and 0.2 M Na_2MoO_4 solution series are similar to each other except for the better resolution at the lower concentration. Some of the spectra of the 0.4 M solutions are shown in Figure 3. In the pH range of 6.5−5, a narrow peak of MoO_4^{2-} (∼0 ppm) and two wider signals (A) previously assigned to $Mo_7O_{24}^{6-}$ are observed.[19,21] Signals A are always observed together and have a constant intensity ratio throughout the pH range, where, according to ^{17}O NMR, heptamolybdate exists. At pH <5 two new broader lines (B) appear and strengthen upon further acidification at the expense of signals A, becoming most developed at pH values of 3−2, where only β-$Mo_8O_{26}^{4-}$ is observed by ^{17}O NMR. Signals B are similar in position and intensity to those of the CH_3CN solution containing β-octamolybdate.[16,17,20,31] The above observations allow us to assign spectrum B to β-$[Mo_8O_{26}]^{4-}$. At pH ≤2 an even broader line, C, centered at 0 to −10 ppm, is observed. It can be attributed to IPA $Mo_{36}O_{112}(H_2O)_{16}^{8-}$, which was identified elsewhere as a predominant species within this acidity range.[12,14,15,22] Upon its acidification to pH <1, line D, strengthening and narrowing with acidity, appears. At the same time it shifts to $\delta = -63$ ppm at $P \approx 4$. Upon further addition of $HClO_4$, up to 6 M concentration the parameters of signal D change insignificantly. In agreement with data on the existence of cationic forms in strongly acidic solutions,[1−3,9,11,22] we have assigned signal D to oxocationic species. The observed dependence of its δ value and width on the acidity indicates the coexistence of different species participating in the intermediate−fast range on the ^{95}Mo NMR time-scale, chemical exchange. As found in the spectrophotometric study of Mo^{VI} equilibria in perchloric acid solutions,[9] two monomeric oxocationic species, $MoO_2(OH)(H_2O)_3^+$ and $MoO_2(H_2O)_4^{2+}$ (or $MoO_2(OH)^+$ and MoO_2^{2+} for short), form successively at [Mo] < 10^{-4} M. The MoO_2^{2+} begins to form in ∼1 N $HClO_4$, its content ≈50% in 6.3 M $HClO_4$ and ∼90% in 8.2 N $HClO_4$. At higher Mo concentrations (2.5 × 10^{-3} M), monomeric $MoO_2(OH)^+$ species were found to dimerize with each other and with MoO_2^{2+}. It is to be noted, however, that the dimers can form until protonated monomers are present in solution. MoO_2^{2+} remains unprotonated at the highest achievable concentration of $HClO_4$; therefore, by itself it cannot dimerize, exactly parallel to the situation of MoO_4^{2-} in alkaline solutions. We suggest that signal D is an averaged signal of at first different dimeric species and then of $Mo_2O_4(OH)^{3+}$ and monomeric MoO_2^{2+}. We were able to measure ^{95}Mo NMR spectra of 0.01 and 0.005 M molybdate solutions in ∼8.3 M $HClO_4$. The signal shift (up to −69 ppm) and narrowing (∼270 Hz) with increase in $HClO_4$ concentration show that the fraction of MoO_2^{2+} gradually increases.

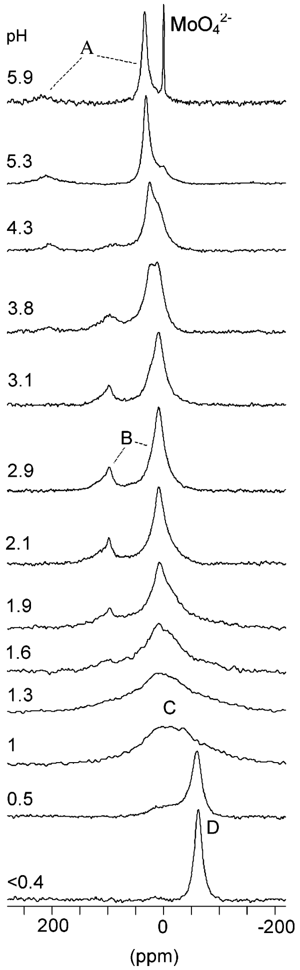

Figure 3. ^{95}Mo NMR spectra of Na_2MoO_4 solutions, [Mo] = 0.4 M, acidified with $HClO_4$, at different pH. The number of scans is up to 10^4, T is 293 K.

To justify the above assignments of the ^{95}Mo NMR signals, it is necessary to consider the IPA structures. Structurally,

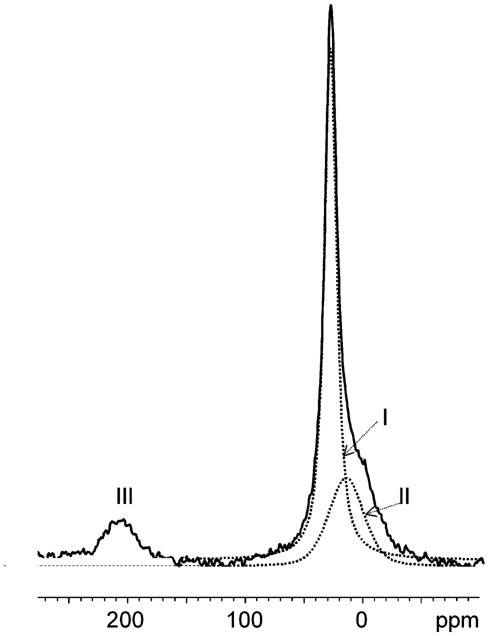

Figure 4. The ^{95}Mo NMR spectrum of $Mo_7O_{24}^{6-}$, [Mo] = 0.5 M, pH ≈ 5, with the decomposition of the major signal.

the heptametalate IPA (M = Mo, W) corresponds to a fragment of the saturated decavanadate structure, $V_{10}O_{28}^{6-}$, and it similarly contains metal atoms of three structural types (Figure 2).[14] The central M_{III} atoms lack for terminal oxygens whereas M_I and M_{II} atoms each have *cis*-dioxo terminal group in heptametalates and a single terminal oxygen in decavanadate. $W_7O_{24}^{6-}$ and $Mo_7O_{24}^{6-}$ have similar ^{17}O NMR spectra confirming their similar molecular and electronic structures in solution, so their NMR spectra measured on W and Mo are expected to be similar as well, except for their different line widths.[18] According to this structure, $W_7O_{24}^{6-}$ has the ^{183}W NMR spectrum, consisting of three peaks with that of atom W_{III} shifted most to higher frequencies.[18] In the ^{51}V spectrum of $V_{10}O_{28}^{6-}$, the signal of atoms V_{III} is also that at the highest frequency (−420 ppm).[35] A similar signal was expected in the ^{95}Mo NMR spectrum of $Mo_7O_{24}^{6-}$ as well, and it was found at $\delta \approx 200$ ppm.[19,21,22] The intensity ratio of two A signals equal to ∼1:6 confirms the assignment of the minor signal to Mo_{III} and the other one to the rest of the Mo atoms. The latter signal is noticeably asymmetric and can be decomposed into two overlapping peaks arising from the Mo_I and Mo_{II} atoms (Figure 4) so that the intensities of the three peaks in spectrum A have a ratio of 1:4:2, in agreement with the structure (Figure 2a). When the pH is lowered, the signals of heptamolybdate shift by ca. −15 ppm and weaken (Figure 3, Table 1). However, the signal of Mo_{III}, not masked by those of the other IPA, is still noticeable even at a pH level of 3.1 for the 0.4 M Mo solution, but its large width (∼1 kHz) does not allow one to accurately determine the content of the IPA in solutions from the intensity of this signal alone.

In β-octamolybdate, where two MO_6 octahedra in the equatorial plane are missing in comparison with the $M_{10}O_{28}$ structure, two central Mo_{III} atoms gain a terminal oxygen (Figure 2b). As a result, their signal shifts by ca. −100 ppm relative to that of the central atom of heptamolybdate. The rest of the six Mo atoms of β-$Mo_8O_{26}^{4-}$, identical with those of $Mo_7O_{24}^{6-}$, each have two terminal oxygens and are observed by the signals in the same δ_{Mo} region as for heptamolybdate, only slightly shifted upfield. The intensity ratio, I_{I+II}/I_{III}, may be a little higher than the expected value of 3:1 because of the overlap of the Mo_{I+II} signals of octamolybdate with those of the other IPA and the error in determining the intensity of broad signals. Still, octamolybdate dominates at a pH of ∼3−2 (Figure 3). Its major signal, at $\delta \approx 10$ ppm, arising from Mo_I and Mo_{II} atoms, is slightly asymmetric as it is a sum of two close lines but it is less evident than for heptamolybdate because of the larger signal widths and overlaps. In addition, the exchange between hepta- and octamolybdates also broadens their ^{95}Mo signals lowering the resolution. Nevertheless, the low-frequency signals of spectra A and B are clearly evident especially at lower Mo concentrations, and their intensities can be approximately evaluated using the deconvolution procedure.

It should be noted that the ^{95}Mo NMR spectrum of β-$Mo_8O_{26}^{4-}$ has not been properly analyzed in the literature.[21−23] In only one case were both of the signals assigned to this IPA.[21] Observing the actual spectrum of β-$Mo_8O_{26}^{4-}$ at the pH of 3, Coddington and Taylor[22] attributed to this IPA only a weaker signal, at 100 ppm, whereas its major peak at 10 ppm was mistakenly attributed to IPA $Mo_{36}O_{112}^{8-}$. This assignment was based on the molecular mass value, measured at a pH of 1.1, where HPA $Mo_{36}O_{112}^{8-}$ actually exists, but the ^{95}Mo NMR signal is already quite different. Howarth et al.[23] attribute the signal at 100 ppm to four Mo_I atoms by analogy with $V_9MoO_{28}^{5-}$, where the Mo atom is in a “capping” position and δ ^{95}Mo is at ∼110 ppm, but they do not discuss which atoms are responsible for the major peak. As a result, they underestimate the content of octamolybdate in solutions (32% at pH ∼3), where, according to the ^{17}O as well as the ^{95}Mo NMR spectra, it is a predominant form (≥80%), and they explain this difference by the presence of a hypothetical IPA $H_3Mo_8O_{28}^{5-}$.[23]

It is seen that with the increase in the number of the terminal M=O bonds in an MO_6 polyhedron, the signals of M in the ^{51}V, ^{183}W, and ^{95}Mo spectra shift to lower frequencies. A similar tendency was observed for the molybdenum heteropolyacids of different types.[24] For Mo in IPA, such a shift is about 100 ppm per one terminal oxygen. Actually, δ ^{95}Mo is equal to ∼200 ppm for Mo without terminal oxygens, as in $Mo_7O_{24}^{6-}$. Mo atoms with one terminal oxygen have a δ of about 100 ppm in β-$Mo_8O_{26}^{4-}$, 120 ppm in hexamolybdate,[17] ∼110 ppm in $V_9MoO_{28}^{5-}$, and ∼130 ppm in $V_2Mo_4O_{19}^{4-}$.[19,36] Mo atoms with two terminal oxygens in hepta- and α- and β-octamolybdates are observed at δ values of ∼30−0 ppm (Table 1). The δ difference within one type of Mo atoms is less in magnitude and depends on the terminal Mo−O bond lengths

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(35) Besecker, C. J.; Klemperer, W. G.; Maltbie, D. J.; Wright, D. A. *Inorg. Chem.* **1985**, *24*, 1027−1032.

(36) Howarth, O. W.; Pettersson, L.; Andersson, I. *J. Chem. Soc., Dalton Trans.* **1989**, 1915−1923.

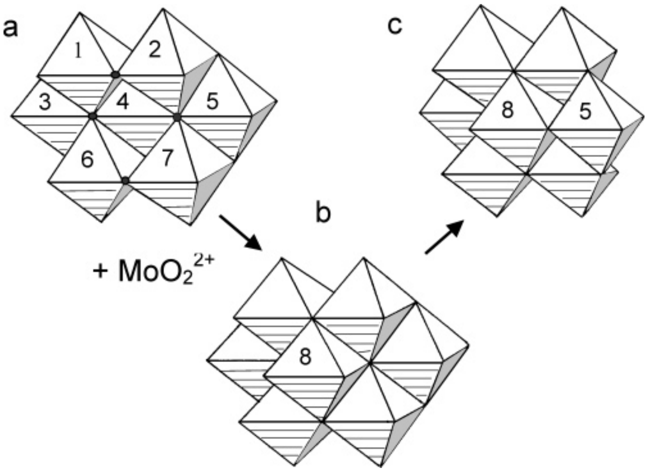

Figure 5. Polyhedral models of the $Mo_7O_{24}^{6-}$ and β-$Mo_8O_{26}^{4-}$ structures and the proposed mechanism of the hepta- to octamolybdate interconversions.

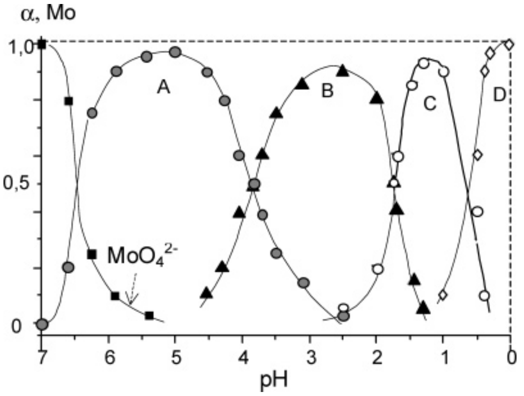

Figure 6. Distribution of Mo species with pH, derived from the ^{95}Mo NMR spectra of 0.4 M solutions of Na_2MoO_4, acidified with $HClO_4$. (A) $H_xMo_7O_{24}^{x-6}$ ($x \sim 0-2$); (B) β-$Mo_8O_{26}^{4-}$; (C) mainly $Mo_{36}O_{112}^{8-}$; (D) cationic species, including MoO_2^{2+}.

or the degree of π-bonding. At protonation of $Mo_7O_{24}^{6-}$ or its conversion into $Mo_8O_{26}^{4-}$, when the oxygen content per one Mo atom decreases, the terminal bonds shorten, which results in a lower-frequency shift of Mo signals. The signal of Mo oxocationic species also having two terminal oxygens is shifted to ca. −60 ppm because of the further shortening of the Mo═O bonds. Therefore, the dependence of δ_{Mo} on the number of the π-bonded oxygen atoms and the degree of the π-bonding is clearly manifested in the ^{95}Mo NMR spectra of the polyoxomolybdates.

According to structural data,[14] IPA $[Mo_{36}O_{112}(H_2O)_{18}]^{8-}$ contains MoO_6 polyhedra with two, one, and no terminal oxygens, such that in the ^{95}Mo NMR spectrum of its solution, several signals in the corresponding δ ranges should be expected. However, the signals are strongly broadened and not resolved because of the too large IPA dimensions.

It was noted elsewhere that $Mo_7O_{24}^{6-}$ and β-$Mo_8O_{26}^{4-}$ have relatively different structures and a rather complicated mechanism of their interconversion through two hypothetical IPAs, $Mo_6O_x^{n-}$ and $H_3Mo_8O_{28}^{5-}$, was proposed.[15,23] However, although the exchange between hepta- and octamolybdates observed by NMR is slow, it suggests their direct interconversions. Such a possibility exists because their structures are actually the fragments of the decametalate structure and do not differ significantly (Figures 2 and 5). In heptamolybdate, there is a cavity in place of the missing central MO_6 octahedron, surrounded by two O_D and two O_A oxygen atoms, clearly seen in the stereoscopic view of the IPA from Evans.[37] O_D atoms are subjected to protonation, which shows their higher negative charge; it is suitable for capturing the MoO_2^{2+} cation, leading directly to the composition of $Mo_8O_{26}^{4-}$. Then, simple jumping of either one of the two $Mo_{II}O_6$ octahedra, which have a rather high mobility within the IPA,[18] into the neighboring position will give the β-octamolybdate structure. In essence, the latter conversion corresponds to the isomerization of octamolybdate, which may be as fast as the α- to β-$Mo_8O_{26}^{4-}$ isomerization.[31] On the whole, the chemical exchange between the two IPAs consists of the following interconversions

$$H_2Mo_7O_{24}^{4-} + H_2MoO_4 \leftrightarrow [Mo_8O_{26}]^{4-} + 2H_2O$$

or shorter

$$Mo_7O_{24}^{6-} + MoO_2^{2+} \leftrightarrow [Mo_8O_{26}]^{4-} \qquad (2)$$

As shown by Voldman et al.,[11] molybdenum(VI) can be extracted from its solutions at pH values of 3−4 as MoO_2^{2+} with a cationic exchanger, which may be heptamolybdate itself.

The ^{17}O and ^{95}Mo NMR spectra of the same concentrated Mo solutions agree well with each other. The higher concentration sensitivity of ^{95}Mo NMR has allowed us to study in detail more dilute solutions, where the spectra resolution is better and from the intensity of the signals we were able to evaluate approximately the percentage of the corresponding species, depending on the pH. The results are shown in Figure 6 as the distribution diagram for 0.4 M Mo solutions. In the diagram the overall content of $H_nMo_7O_{24}^{n-6}$ (n = ca. 0−2) is shown. We can argue that there is no NMR evidence for the existence of an intermediate species between heptamolybdate and octamolybdate and instead, that the formation of diprotonated heptamolybdate can be suggested, taking into account that two different sites, the triply bridging O_B and doubly bridging O_D oxygen atoms, are protonated. These conclusions are in agreement with some previously suggested equilibria schemes.[10] Although the composition of IPA $Mo_{36}O_{112}^{4-}$ could not be confirmed by NMR, its content, possibly combined with another unidentified large IPA, was approximately estimated by the intensity of the broad line, in order to follow the IPA conversion into cationic species.

Conclusion

For the first time the ^{95}Mo NMR spectra of aqueous molybdate solutions have been systematically measured over a wide range of acidity. A correlation was found between the ^{95}Mo NMR parameters and the molybdenum structural characteristics. This can be used in studying different molybdenum-containing complexes comparable in dimension

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with octamolybdate, which provides acceptable signal widths and resolution. Contrary to the opinion that the high mobility of the molybdenum IPAs and intra- and intermolecular exchange in aqueous solutions averages their ^{95}Mo NMR spectra,[22,23] making them uninformative, it was found that the spectra of $Mo_7O_{24}^{6-}$ and β-$[Mo_8O_{26}]^{4-}$ are characteristic and can serve as their fingerprints. Compared with previous works, the aqueous molybdate solutions are actually studied in parallel on both titled nuclei. For the first time, the ^{17}O NMR spectrum of β-octamolybdate is measured at its natural ^{17}O content, which is significant for the proper spectrum interpretation. It is found from analysis of the ^{17}O spectra, measured at gradual changes of pH between 5.5 and 2.5, that only heptamolybdate and octamolybdate exist in this acidity interval and that the chemical exchange occurs between them. From the ^{17}O NMR spectra, two protonation sites of $Mo_7O_{24}^{6-}$ have been confirmed. Acidification by the electrodialysis method provided minimum Na content, which allowed us to avoid the precipitation of molybdenum and to work with natural ^{17}O content.

Supporting Information Available: ^{95}Mo ^{17}O NMR spectral information in PDF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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