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Rates of Isotopic Oxygen Exchange with Solvent and Oxygen Atom Transfer Involving $[Mo_3O_4(OH_2)_9]^{4+}$

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Mo(IV) in aqueous acidic media exists as $Mo_3O_4^{4+}$(aq). The structure is retained in dilute (10^{-3} M) solution, in the SCN^- and $C_2O_4^{2-}$ complexes, and in the hydroxide precipitate. The half-time for isotopic oxygen exchange with solvent at 25 °C is about 5 days for the capping oxygen, >3 years for the bridging oxygens, and 1.1 h for the water trans to the capping oxygen. The waters trans to the bridging oxygens exchange with a half-time of approximately 20 min at 0 °C. The X-ray structure of $[Pt(en)_2][Mo_3O_4(ox)_3(OH_2)_3]\cdot 3H_2O$ is presented in conjugation with the ^{18}O-exchange studies. The effect of complexation on the water-exchange rate is discussed. Reduction of $Mo_3O_4^{4+}$(aq) to Mo^{III}_3 or $Mo^{III}_2Mo^{IV}$ and reoxidation with O_2 showed at least 95% retention of four oxygens. The rate of oxygen exchange of $Mo^{III}_3(O)_4^{n+}$ with solvent is shown to be very slow. Exchange was not observed over a period of 2 months at room temperature.

Introduction

The structure and kinetic properties of molybdenum oxy ions in aqueous, noncomplexing, media is of continuing interest and of practical importance. The aquomolybdenum(IV) ion was first described in 1966 by Souchay,[1] and several formulas and structures have been proposed[2]. X-ray structure studies of complexes derived from the aquo ion often showed a trimeric oxo-bridged basic unit suggesting that this grouping was also present in the aquo ion.[3,6] Direct proof of the trimeric nature of the Mo(IV) aquo ion was provided in 1980 in a preliminary note.[4] These isotopic ^{18}O-transfer studies were coupled with an X-ray crystal structure determination[5] and unambiguously demonstrated that the $Mo_3O_4^{4+}$(aq) trimer was essentially the sole species present at equilibrium even in dilute (10^{-3} M) solution and that the kinetics of opening the structure even in 1 M acid was very slow (i.e., $t_{1/2}$ > 3 days at room temperature). From these studies, nothing was established about the number or the kinetic properties of the coordinated waters presumed associated with $Mo_3O_4^{4+}$(aq). The purposes of this paper are to provide more detailed information about the zero-time oxygen transfer between the Mo(IV) aquo ion and two of its complexes, to interpret kinetic results on the ^{18}O exchange on the two types of oxo bridges, to present the first kinetic determination of the ^{18}O exchange between solvent and both types of coordinated water, and to describe and interpret studies on oxygen atom transfer during reduction and reoxidation of Mo(IV). These studies support the conclusion that the kinetic and thermodynamic stability of the Mo(IV) trimer are very large and dominate the chemistry of this oxidation state of Mo. In order to more easily describe the types of oxygen in this ion we will utilize Figure 1 and the labels contained therein although, at the beginning of this study, the composition and structures were unknown.

Experimental Section

Stock solutions of $Mo_3O_4^{4+}$(aq) under oxygen-free nitrogen were prepared from the stoichiometric amounts of $Na_2MoO_4\cdot 2H_2O$ and K_3MoCl_6 (reagent grade) in 2.0 M HCl by reaction at 80 °C. The reaction was complete in 2 h and gave a nearly quantitative yield. These solutions, held in serum bottles under nitrogen, were stable for several months. Immediately before use, the ion was purified by ion-exchange chromatography. For this purpose a 1.0-cm diameter column of 10-cm length was saturated to about 30% capacity with the diluted stock solution. After being washed with a small quantity of very dilute acid, it was treated with a large amount of 0.5 M acid of the type desired to remove the yellow $Mo_2O_4^{2+}$, the main impurity, and then the ion of interest, $Mo_3O_4^{4+}$, was eluted with 3–4 M acid.

$(CH_3)_4N(SCN)$ was prepared from NaSCN by ion-exchange methods and recrystallized from a 1:1 (v/v) methanol–water mixture. All normal water was distilled and doubly deionized. The ^{18}O water was distilled once from alkaline MnO_4^-, once from acidic $Cr_2O_7^{2-}$, and twice by itself. It was normalized with respect to ^2_1H. Ion-exchange separations were made on columns of Dowex 50W-X exchange resin of 100–200 dry mesh with appropriate length and diameter.

Temperature was maintained to ±0.02 °C with a thermostated bath. At 0 °C, an intimately mixed water–ice bath in a Dewar flask was used that did not vary by more than 0.05 °C.

Isotopic ^{18}O determinations were carried out on highly purified CO_2 utilizing the 46/(44 + 45) *m/c* ratio, which was measured on a dual-collector Nuclide isotope ratio mass spectrometer. Solid complexes, containing oxygen in several forms, were sealed with $Hg(CN)_2$ in glass tubes under $\leq 10^{-4}$ mm pressure and heated for 1 h at 425 °C. The contents, which were volatile at −78 °C, were deposited in a preparative gas chromatographic apparatus, and the CO_2 was separated on a silicone oil–firebrick column. The 46/(44 + 45) ratio was compared to a standard CO_2 sample that was arbitrarily given the value 4.00×10^{-3}. Low enrichments were used, less than 4 times normal, so the ratio was within the region of linearity. The solvent water was measured by equilibration with CO_2 and by direct reaction with $Hg(CN)_2$, and the agreement was satisfactory.

In order to carry out measurements of the holdback of oxygens from exchange by the metal ion or oxygen-transfer experiments or kinetic determination of oxygen exchange, it is necessary to be able to bring the metal ion, with the oxygens of interest in the first coordination sphere, out of solution in a pure solid with uniform composition. No suitable precipitating agent has ever been found for Mo(IV) except for the hydroxide, which is not crystalline and is of varying water content. In order to overcome this handicap, we utilized two complexes of Mo(IV) formed with SCN^- and oxalate ion. A large excess of SCN^- rapidly forms a series of complexes, eventually leading to $[Mo_3O_4(SCN)_9]^{5-}$. As we will show later, six waters are replaced rapidly and three a little more slowly, but the important point is that the core oxygens are not replaced even with long periods of contact with the solvent. With $(CH_3)_4N^+$ present in excess, the complex is precipitated within a few minutes at 0 °C and has excellent properties for ^{18}O analysis. It was used to determine the formula of the core and the rates of oxygen exchange within that core. The oxalate complex was also used in those studies, but its main use was in determining the rate of water exchange with one type of coordinated water. A previous crystal structure of the oxalate complex had been done and showed one set of unique waters to be present (the oxalates occupying the other type of water position, type D).[6] However, that structure was done on crystals obtained after long standing, and it could not be assumed that rearrangement had not occurred. Thus, we formed the complex very rapidly (~30 s, 0 °C) and precipitated it immediately (within 15 s) and established that it had the same composition as $[Pt(en)_2][Mo_3O_4(ox)_3(OH_2)_3]\cdot 3H_2O$ single crystals that were slowly crystallized. Thus, the single-crystal X-ray structure of the oxalate complex given in this paper provides strong evidence that the waters whose exchange is being studied are indeed those trans to the capping oxygen.

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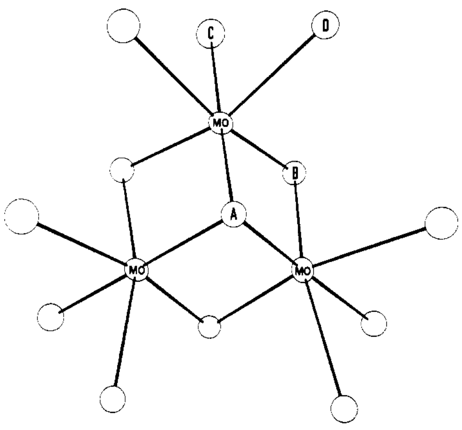

Figure 1. $[Mo_3O_4(OH_2)_9]^{4+}$: A, B = O; C, D = OH_2.

The preparation of $[(CH_3)_4N]_5[Mo_3O_4(SCN)_9]$ used for ^{18}O studies was accomplished simply by adding a large excess of solid $(CH_3)_4N(SCN)$ to a solution of Mo(IV) > 0.05 M in 0.5–4 M acid. Within 1–2 min at 0 °C the precipitate formed. It was allowed to remain in contact with the mother liquor for 15–20 min and collected on a filter. After being washed with a methanol–ether mixture and with ether, it was dried under vacuum (10^{-5} mm) for several hours. Forming suitable crystals for X-ray analysis was difficult. Finally, small, well-formed crystals were obtained from saturated acetonitrile–H_2O mixtures by slow cooling. Since the solutions from which the crystals were deposited did not have excess SCN^- present, some dissociation occurred and the formula of the material finally obtained had a water substituted for one of the thiocyanates. The X-ray powder pattern for the product obtained by rapid methods, in those samples used for oxygen-retention studies, agrees with that from ground up samples of the crystalline salt. Analysis of a typical product obtained by rapid precipitation is given in Table III.

The crystals used for X-ray analysis of the tris(oxalato) complex were prepared by allowing a dilute mixture of $[Pt(en)_2]^{2+}$ and $[Mo_3O_4(C_2O_4)_3(OH_2)_3]^{2-}$ to set for several days at room temperature. From 0.5 M acid the deep red $[Pt(en)_2][Mo_3O_4(ox)_3(OH_2)_3]\cdot 3H_2O$ crystals were well formed and of suitable size.

To show that the solid samples, produced by rapid precipitation, were the same as the single crystals whose structure had been completed, their density was determined by the flotation method (CCl_4 + CHI_3) and the equivalent weight by Ce(IV)–Fe(II) titration. Both were in agreement with the values calculated on the basis of the crystallographic results (see Table III).

Space group and unit cell dimensions were determined by a least-squares refinement of the angles of 25 automatically centered reflections. Least-squares refinement resulted in a final conventional *R* factor of 0.036.

Proof of the trimeric nature of Mo(IV) came first from oxygen-transfer experiments. To a cooled acidic solution of Mo(IV) was added ^{18}O water at 0 °C. Within a few seconds a saturated NaSCN solution at 0 °C was added. After about 10 min, addition of excess solid $(CH_3)_4N(SCN)$ produced the desired precipitate. After 1–45 min at 0 °C (up to 1 day had no isotope dilution effect), the product was collected on a filter, washed twice with 2-propanol and twice with anhydrous ether, and dried for 12 h under vacuum (10^{-5} mm). It was then treated in the usual manner to convert its oxygen to CO_2.

The structural stability of the Mo_3O_4 moiety in nearly neutral solution where it precipitates as a hydroxide was investigated. A sample of $Mo_3{}^{18}O_4{}^{4+}$(aq) was equilibrated with normal water for a short time so that the ^{18}O enrichment was only in the capping and bridging oxygens. The coordinated waters were normal. A portion of this solution was complexed with ox^{2-} and precipitated as $[Pt(en)_2][Mo_3O_4(ox)_3(OH_2)_3]\cdot 3H_2O$. The remainder of the solution was brought to slightly above pH 5 where a greenish black precipitate formed. Air oxidation was not usually a problem because of the short times involved. Half of the precipitate was redissolved in CH_3SO_3H, purified by ion exchange, verified spectrally to be $Mo_3O_4{}^{4+}$(aq), complexed with ox^{2-}, and precipitated with $[Pt(en)_2]^{2+}$. The samples were sealed under vacuum (10^{-4} mmHg) and converted to CO_2, and the CO_2 was analyzed for ^{18}O content.

^{18}O Water Exchange Kinetics

A. Capping Oxygen (Type A). The initial studies were undertaken to measure the number of the oxygens within the core fastest to exchange. For this purpose the SCN^- complex was used because nearly all of the waters are displaced and only those in the core remain in the solid isolated. It was fortunate that a wide separation in exchange rates exists between the two types of core oxygens so overlap is negligible. In the most definitive experiments Mo(IV) was prepared in ^{18}O water and separated on an ion-exchange column using normal solvent that left ^{18}O in only the A and B positions. The total ^{18}O content of $((CH_3)_4N)_5[Mo_3O_4(SCN)_9]$ produced by SCN^- coordination was then followed as a function of time via the method described earlier. Plots of R_N vs. time leveled off at values that corresponded to 1.00 ± 0.05 of the four possible oxygens exchanging. Using the experimental infinity point, graphs of $-\ln(1 - F)$ vs. time, from which the observed rate constant could be obtained, were linear out to 6 half-times. The number of rapidly exchanging core oxygens was also obtained in the reverse direction with normal $Mo_3O_4{}^{4+}$(aq), enriched water, and the SCN^- method.

B. Bridging Oxygen (Type B). For the oxygens of type B, bridging oxygens, the rate was much too slow to follow to any major extent. In this case, higher enrichments in the core were used, and although the rates were followed for long periods, only small changes were observed. Since the ∞ value was that of normal water and was well-known, the rate constant could be evaluated with reasonable accuracy even though only a small fraction of the exchange was followed. It should be pointed out here that, because of the long times involved, the temperature was not maintained at 25 °C. Rather, it was the average room temperature in a shielded portion of the air-conditioned mass spectrometer room, i.e., ~22 °C.

C. Water Trans to Capping Oxygen (Type C). Exchange of the waters trans to the capping oxygen (type C) was studied by following the decrease in ^{18}O content in the oxalate complex. A large sample of Mo(IV) stock was diluted with 0.5 M CH_3SO_3H, allowed to aquate for about 8 h (to remove chloro complexes), and placed on an ion-exchange column. It was washed with 0.5 M CH_3SO_3H to remove Mo(V) and other impurities and was eluted with 5 M CH_3SO_3H. After dilution to 1.0 M acid with ^{18}O-enriched water, it was allowed to equilibrate for 4 h at 22 °C. This allowed ample time for isotopic equilibration between coordinated and solvent water. A sample of the solvent was retained for isotopic analysis. After dilution, the solution was again applied to an ion-exchange column in the H^+ form at 0 °C and the ^{18}O-containing solvent removed by washing with 0.5 M CH_3SO_3H in normal water (0.5 M HCl for the Cl^- studies). The Mo(IV) was removed from the column with 5 M CH_3SO_3H (4 M HCl for Cl^- studies) and collected in an ice bath. A small sample was taken for acidity analysis. Known volumes of the Mo(IV) solution were diluted with normal water and with a standard $NaSO_3CH_3$ (or NaCl) solution to give the desired concentration and ionic strength. The solutions, now containing Mo(IV) having normal oxygens in the core, ^{18}O enrichment in the coordinated waters (at least type C waters), and normal solvent, were brought to the proper temperature and aliquots taken at appropriate times to follow the rate of exchange. The time zero values were used to determine the number of waters of type C. Each aliquot was applied to a short ion-exchange column (H^+ form) and "pushed off" with 0.5 M $H_2C_2O_4$ solution. Addition of a saturated $[Pt(en)_2]Cl_2$ solution (2–3 drops) gave an immediate crystalline precipitate that was collected by centrifugation, washed three times with ice cold methanol and two times with peroxide-free ether, and dried under a stream of N_2. In the neutral region, an excess of oxalate ion prevented rapid deposition of the crystalline solid due presumably to its coordination at the other water positions.

Measuring the type C water-exchange rate on $[Mo_3O_4(ox)_3(OH_2)_3]^{2-}$ was more difficult because of two problems. First, oxygen exchange with coordinated oxalate ion occurred in the more acidic regions, and second, we have no quantitative knowledge concerning the association constants between oxalate and $Mo_3O_4{}^{4+}$ and thus do not know what fraction of the oxalate ion is uncoordinated.

Attempts were made to measure the rate of type C water exchange in the presence of excess oxalate ion in an ^{18}O-enriched, slightly acidic medium. Oxygen exchange between coordinated oxalate ligands and the solvent medium caused difficulties in data interpretation. On the basis of ^{18}O-exchange data for the oxalate ion,[7] it was calculated that at pH 4 exchange on uncoordinated oxalate ion would be slow and not interfere with our measurements. Numerous runs were attempted under these conditions, but in the presence of excess oxalate ion at this acidity the complex ion would not precipitate. A solid of similar appearance could be precipitated from a 1:1 CH_3CN-H_2O mixture, but the sample enrichment at infinite time never came to the value calculated from the solvent enrichment. This suggested that there were less than three oxygens exchanging over the time of the experiment and/or that there were more normal oxygens in the compound than it was thought to contain. The difference between the calculated and observed enrichments at infinite time was somewhat inconsistent. The only variable of any magnitude in these investigations was the free oxalate ion concentration. This was not controlled, and since it exists as 39% $C_2O_4^{2-}$ and 61% $HC_2O_4^-$ at pH 4, it is not inconceivable that solids with varying degrees of oxalate coordination could have been precipitated from the CH_3CN-H_2O mixture. At this point another method for following type C water exchange on $Mo_3O_4^{4+}(aq)$ was designed and implemented. Despite the discrepancy between the calculated and observed infinity values, the observed rate constants from these earlier data agree rather well with those obtained later via the modified method. Thus, after a series of preliminary runs we chose to isolate the pure oxalate complex as the $[Pt(en)_2]^{2+}$ salt, convert it to the highly soluble sodium salt, i.e. $Na_2[Mo_3O_4(ox)_3(OH_2)_3]$, and make measurements on it. In order to assure the maximum ox^{2-} coordination and the least oxygen exchange with ox^{2-}, the studies were conducted in the near-neutral region. Thus, purified, water-enriched Mo(IV) was prepared, converted to the oxalate complex, and precipitated with $[Pt(en)_2]^{2+}$. This solid was stirred with an ion-exchange resin in the Na^+ form to solubilize it, and the pure complex ion solution was treated with acid and salt to give the desired acidity and ionic strength. All of the above operations were carried out as quickly as possible at 0 °C. At this point the solution contained $[Mo_3O_4(ox)_3(^{18}OH_2)_3]^{2-}$ in normal solvent, with only the coordinated waters enriched. After the temperature was quickly raised to the desired level, samples were taken at time intervals and acidified at 0 °C and the complex ion precipitated (nearly quantitatively) with $[Pt(en)_2]^{2+}$. After being washed, dryed, and evacuated in the usual manner, the solids were analyzed for ^{18}O content.

D. Water Trans to Bridging Oxygen (Type D). Noting the observation[8] that, under certain conditions, $Mo(CN)_8^{4-}$ precipitates uncomplexed Mo(IV), we attempted to develop a method for measuring the rate of water exchange of the D type waters. It was presumed that the $t_{1/2}$ for exchange would be shorter than for any of the other oxygens because SCN^- and ox^{2-} substitute in those positions rather rapidly. In this case, normal $Mo_3O_4^{4+}(aq)$ in 1.0 M CH_3SO_3H at 0 °C was treated with small amounts of ^{18}O water at 0 °C, and at selected times, aliquots were injected into a centrifuge tube containing a large excess of solid finely powdered $K_4Mo(CN)_8 \cdot 2H_2O$ whereupon a brownish crystalline precipitate was obtained. It was collected, washed with alcohol and ether, dried with a stream of N_2, and analyzed for ^{18}O content.

E. Oxygen Transfer in Reduction and Reoxidation. It has been conclusively demonstrated that $Mo_3O_4^{4+}(aq)$ can be completely reduced to Mo^{III}_3, which probably is trimeric, or to $Mo^{III}_2Mo^{IV}$, also thought to be trimeric.[9,10] These experiments were designed to see to what extent the oxygens in the Mo(IV) core were retained when reduced to either of the two lower oxidation state ions.

Enriched samples of $Mo_3O_4^{4+}(aq)$ were allowed to aquate in normal water until only types A and B were enriched and to essentially the same extent. Reduction was accomplished electrolytically at a mercury-pool electrode under an O_2-free atmosphere. After about 2 h the orange-brown $Mo^{III}_2Mo^{IV}$, identified by its UV–visible[9] spectrum, was the predominant species present. It was oxidized with O_2, purified by ion-exchange chromatography, converted to the oxalate complex, precipitated with $Pt(en)_2^{2+}$, and analyzed for ^{18}O content.

Table I. $Mo_3O_4^{4+}$ Core-Oxygen Transfer to (TM)MoSCN

max time of exch,[a] h	10^3R_N(Mo–O) (initial)	10^3R_N-((TM)MoSCN)[b]	no. of trials
0.10[c,e,h]	3.98	4.06 ± 0.05[i]	8
0.15[d,f,h]	13.30	12.15 ± 0.25	6
0.25[d,f,h]	8.331	8.296 ± 0.08	7
0.50[d,e,h]	12.82	12.68 ± 0.07	4
0.15[d,e,g]	8.302	8.18 ± 0.05	3

[a] Exchange time with solvent + contact time with solid. [b] ((TM)MoSCN) = $[(CH_3)_4N]_5[Mo_3O_4(SCN)_9]$. [c] Solvent: $9.28 \times 10^{-3} = R_N$. [d] Solvent: $3.92 \times 10^{-3} = R_N$. [e] $T = 0$ °C. [f] $T = 26$ °C. [g] Recrystallized from CH_3CN, excess SCN^-. [h] Finalized procedure. [i] ± value is 1σ.

Table II. $Mo_3O_4^{4+}$ Core-Oxygen Transfer to $[Mo_3O_4(ox)_3(OH_2)_3]^{2-}$

max time of exch, days	10^3R_N(Mo–O)[a] (initial)	10^3R_N-(complex)[b]	no. of trials
0.04	8.072[a]	4.942 ± 0.010	3
0.03	8.303[a]	4.998 ± 0.004	3
0.10	8.161[b]	4.933 ± 0.020	2
0.10	8.161[c]	4.814 ± 0.021	2

[a] Precipitating agent: a, $[Co(en)_3]^{3+}$; b, $[Pt(en)_3]^{4+}$; c, $[Pt(en)_2]^{2+}$. Oxalate complex was formed in 0.12 M H_2ox. [b] $10^3R_N(H_2O) = 3.98$; $10^3R_N(ox^{2-}) = 4.02$.

Similar experiments were carried out with extensive reduction to Mo^{III}_3 (as shown by visible–UV spectra) followed by O_2 oxidation back to $Mo_3O_4^{4+}(aq)$. In one case the reduced solution was held in the reduced state for 2 months before being oxidized. Some air oxidation occurred during this period, but this seemed to give predominantly Mo(V) dimer, which was removed in the ion-exchange purification. Estimated yields of Mo^{IV}_3 were always greater than 70% of the total.

F. Kinetic Data Treatment. The overal rate of exchange for waters of type C follows the equation

$$R = k_{obsd}(3AB/(3A + B))$$

where $k_{obsd} = \ln [[(R_0 - R_\infty)/(R_t - R_\infty)]/\text{time}]$, R_0, R_t, and R_∞ are the ^{18}O ratios at the subscribed times, $A = [Mo_3O_4^{4+}(aq)]$, and $B = [H_2O]$. Since $B \gg 3A$, $R = k_{obsd}3[A] = k[A]$ or $k = k_{obsd} \cdot 3$. This also applies to the bridging oxygens, but for the capping oxygen $k = k_{obsd}$. No corrections were made for the minute isotope effect.

Results

Demonstration of Trimeric Structure. The proof consists of showing that from a solution containing $Mo^{IV}(aq)$ and solvent of different ^{18}O content a solid complex salt of Mo(IV) can be made and rapidly brought out of solution without appreciable solvent exchange of some of its first coordination sphere oxygens. The core structure in solution must then contain at least those oxygens found (by X-ray crystal studies) in the solid complex ion. Further, if this can be done reversibly, that is, oxo aquo → to isolated complex → to oxo aquo ion → to complex without the loss of enrichment in the core oxygens, then the Mo–O core found in the solid must be kinetically stable in solution and capable of being complexed without major structural change.

Table I lists the experiments carried out that establish these points. The first entry gives the average of the trials using normal complex enriched water using the final optimized method. The bulk of the runs utilized enriched complex in order to conserve ^{18}O water. A problem existed for a long time that was not completely understood until late in the study (after the crystal structure was done). There was always a small, 3–5% contribution from the solvent to the oxygen in the complex that was independent

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Table III. Analysis of Compounds

$[Pt(en)_2][Mo_3O_4(ox)_3(OH_2)_3]\cdot 3H_2O$ (fw 985.27)

	C	H	N	equiv wt	density, g/cm^3
calcd	12.18	2.25	5.68	74.2	2.494
found	11.99	2.89	5.45	75.7	2.480

$[Co(en)_3][Mo_3O_4(ox)_3(OH_2)_3]Hox$ (fw 998.17)

	C	H	N	equiv wt
calcd	16.83	3.13	8.42	71.3
found	16.62	3.91	8.28	80.0

$[Pt(en)_3][Mo_3O_4(ox)_3(OH_2)_3](Hox)_2$[a]

	C	H	N
calcd	15.70	2.64	6.87
found	15.15	3.07	6.13

$[(CH_3)_4N]_4[Mo_3O_4(NCS)_8(OH_2)]\cdot 3H_2O$ (fw 1185.1)

	C	H	N	S	Mo	O	equiv wt
calcd	24.32	4.76	14.18	21.64	24.29	10.80	197.5
found	23.46	4.76	13.04	19.86	24.10	10.01	178.1
	23.73	4.44	13.20			10.27	

$[(CH_3)_4N]_5[Mo_3O_4(NCS)_9]$ (fw 1245.2)

	C	H	N	S
calcd	27.97	15.75	4.86	23.17
found	28.53	15.42	5.09	21.75

[a] Prepared as in the bulk of the ^{18}O measurements.

Table IV. $Mo_3O_4^{4+}$–H_2O Exchange (1.0 M CH_3SO_3H; (Normal $Mo^{IV}O$; Enriched H_2O)[a]

exch time, min	10^3R_N-((TM)Mo(SCN))	10^3R_N-(solvent)
34	3.926[d]	9.61[b]
60	3.916	9.8[c]
108	3.913	9.8[c]
412	3.919	9.8[c]

[a] 0 °C; $R_N(Mo-O) = 3.92 \times 10^{-3}$; isolated by filtration as (TM)MoSCN. [b] Measured by equilibration with CO_2. [c] Calculated on the basis of mixing proportions. [d] Small amount of $(CH_3)_4N(SCN)$ used.

Table V. O Exchange between Dissolved (TM)Mo(SCN) and Water

exch time, h	10^3R_N-((TM)Mo(SCN))[b]	10^3R_N-(solvent)
Normal $Mo^{IV}O$; Enriched H_2O[a]		
24	4.20	13.3[c]
32.5	4.27	13.3[c]
23	3.96[e]	11.04[c]
Enriched $Mo^{IV}O$; Normal H_2O[f]		
360	7.02[e]	
360	7.03[e]	

[a] 26 °C; $R_N(\text{complex}) = 3.92 \times 10^{-3}$; 0.1 M CH_3SO_3H; precipitated with $(CH_3)_4N(SCN)$. [b] After recovery. [c] Measured by CO_2 equilibration. [d] Calculated on the basis of makeup. [e] NaSCN added and then $(CH_3)_4NBr$ or $(CH_3)_4N(SCN)$. [f] $10^3R_N(Mo-O) = 8.20$; $10^3R_N(\text{solvent}) = 3.92$.

Table VI. Core-O Transfer from One Complex, through $Mo^{IV}(aq)$, to Another Complex[a]

$Mo\text{-}1 \rightarrow Mo^{IV}(aq) \rightarrow Mo\text{-}2$

Mo-1	Mo-2	10^3R_N calcd for 100% transfer	10^3R_N calcd for 0% transfer	10^3R_N-(exptl)[b]
ox^{2-}	ox^{2-}	7.77	4.06	7.79
ox^{2-}	SCN^-	8.42	3.97	8.40
SCN^-	ox^{2-}	4.86	4.06	4.86
SCN^-	SCN^-	7.61	3.97	7.59

[a] 26 °C. [b] MoSCN precipitated as the $(CH_3)_4N^+$ salt; Mo(ox) precipitated as the $[Co(en)_3]^{+3}$ salt.

of contact time. This comes from the incomplete formation of $Mo_3O_4(SCN)_9^{5-}$ from the aquo ion before it is precipitated. The precipitate is more closely approximated by the ion with eight SCN^- and one H_2O in the coordination sphere. This was demonstrated by the careful analysis (Table III) on samples made in a fashion identical with those used in the ^{18}O study. In the final series of experiments (Table I) the complex ion $Mo_3O_4(SCN)_9^{5-}$ was allowed to form completely at 0 °C by using an excess of NaSCN before it was brought out of solution with the $(CH_3)_4N^+$ ion. Then, less than 2% apparent exchange with the solvent was uniformly found.

Table II summarizes some of the results of core-oxygen exchange on $Mo^{IV}(aq)$ using the oxalate complex. The composition of the complexes is given in Table III with $[Co(en)_3]^{3+}$, $[Pt(en)_2]^{2+}$, and $[Pt(en)_3]^{4+}$ as precipitating reagents. The number of noncore oxygens was determined from the R_N values at zero time and agreed with the elemental analysis. In all cases the solvent, coordinated waters, and the oxalate ion oxygens were normal so no ambiguity exists due to the unknown (at that time) rates of coordinated water exchange. The values obtained from the R_N values of the precipitated complexes were very similar to those obtained with the thiocyanate complex, but a little more variable. Probably this variability was due to uneven drying of the samples since the coordinated water was very slowly removed under vacuum and was always partially removed under the experimental conditions employed. The enrichment in the product was also smaller due to the oxygen contributed by the oxalate ion, which led to lower precision. Thus, these results using the ox^{2-} complex confirmed those obtained with the SCN^- complex but were not as precise.

Similar experiments established that the $Mo_3O_4^{4+}$ oxygens do not exchange noticeably (in 1–2 days) when either the solid SCN^- or ox^{2-} complexes remain in contact with the solvent, when the complexes are recrystallized from water or CH_3CN at/or below 35 °C, when the complexes are collected on or eluted from ion-exchange resins, or when the acidity changed in the pH range 1–7. Table IV shows the results of a short study to measure the rate of exchange at 0 °C. It clearly shows no discernible exchange of the $Mo_3O_4^{4+}$ entity in 400 min in 1.0 M acid. A similar study in HCl resulted in the same conclusion. Table V gives the results of a study to estimate the rate of oxygen exchange on the thiocyanate complex (0.1 M) at longer times and at 26 °C. The first two entries show considerable apparent exchange, but when compared with the third entry, it is clear that this is due to incomplete SCN^- substitution for water in the isolated complex and in 1 day at 26 °C no exchange was observed. The last two entries show considerable exchange at much longer exchange times and actually are close to the value expected for the complete exchange of one oxygen ($10^3R_N = 7.13$). On the basis of this alone, one cannot conclude anything about the number of oxygens exchanging or the rate of exchange, but these values are consistent with the conclusions reached later regarding the long-time exchange rates of the core Mo(IV) oxygens. Table VI gives a set of representative results on the ^{18}O retention upon conversion from one complex, through the aquo ion, to the same or another complex. Of course, the aquo ion cannot be measured directly for ^{18}O content as explained earlier so only the R_N values for the end members are given. Clearly the experimental values are very close to those calculated for 100% transfer, and one comes to the conclusion that the oxalate ion dissociates (and is precipitated by Pb^{2+}) and the SCN^- dissociates (and is removed as $HgSCN^+$) with retention of the $Mo_3O_4^{4+}$ entity and no appreciable (±2%) exchange is caused by ligand dissociation, complexation, or absorption of $Mo_3O_4^{4+}$ on an ion-exchange resin. In these studies the aquo ion was shown to be the only final product obtained upon removal of the ligands by its ion-exchange properties and its visible

Table VII. $Mo_3O_4^{4+}$–H_2O Exchange Rates (Type A)

Part A

time, h	10^3R_N- (25 °C)	10^3R_N- (40 °C)	time, h	10^3R_N- (25 °C)	10^3R_N- (40 °C)
0	4.998	4.998	241	4.860	4.792
16	4.940	4.984	499	4.852	4.750
91	4.950	4.929	818	4.832	4.726
220	4.881	4.804			

Part B[a]

time, days	10^3R_N[b]	precip ion[c]	time, days	10^3R_N[b]	precip ion[c]
0.8	4.936	1	10.0	4.812	1
	4.962	1		4.773	2
	4.936	1		4.696	3
1.7	4.959	1	17.0	4.742	1
7.0	4.818	1		4.765	2
				4.762	3
			23.0	4.746	1

Part C

temp, °C	$[Mo_3O_4^{4+}]$, M	$[H^+]$, M	complex	$t_{1/2}$, days	10^6k, s^{-1}
0	0.14	1.1	SCN^-	5.8	1.4
30	0.12	1.0	ox^{2-}	4.1	2.0
35	0.08	0.8	SCN^-	3.5	2.3
35	0.10	1.2	ox^{2-}	3.5	2.3

[a] All data at 25 °C. [b] t_∞(all oxygens) = 10^3R_N = 4.030; t_∞(one oxygen of four) = 4.732. [c] Key: 1, $[Co(en)_3]^{3+}$; 2, $[Pt(en)_3]^{4+}$; 3, $[Pt(en)_2]^{2+}$.

Table VIII. $[Mo_3O_4]^{4+}$–Oxygen Exchange (Type B)[a,b]

time,[c] days	10^3R_N	time,[c] days	10^3R_N	time,[c] days	10^3R_N
10	4.810	49	4.722	499	4.668[e]
17	4.742	66	4.717	534	4.664[e]
23	4.746	469	4.704[e]	∞ estimated	4.010[e]

[a] Converted to the oxalate complex for measurement. [b] $T = 24$ °C (approximate). [c] After 10 days essentially all of the type A oxygen is normal. [d] 1.1 M CH_3SO_3H; $[Mo_3O_4^{4+}] = 0.05$ M. [e] These later samples contained appreciable Mo(V) that was separated before ^{18}O determination.

absorption spectrum ($\epsilon = 62.8$ at 505 nm.). Thus, in a preliminary paper we concluded that Mo(IV) exists in noncomplexing aqueous solution as the $Mo_3O_4^{4+}$(aq) ion and that the core oxygens exchange very slowly in the pH range 0–6.[4]

Exchange Rate: Capping Oxygen, Type A. An obvious question then arises concerning the oxygens of $Mo_3O_4^{4+}$. Are there two types of oxygen (with respect to exchange)? If there are two types, which is the faster to exchange? The data in Table VIIA help to answer these questions. They show the change in R_N as a function of time for the $Mo_3O_4^{4+}$–H_2O exchange at two temperatures. Although the changes are small, there is a gradual loss of enrichment that becomes very slow beyond about 5–10 days. This is more clearly shown in Table VIIB. While the experimental error is large compared to the changes expected (±25% for k_{obsd}), it is clear that the number of oxygens is one (out of four) and that the half-life is about 5 days. All three precipitating agents gave the same behavior. Results of the five studies to quantitatively measure this rate are given in Table VIIC. As the data suggest, it is reasonably certain that the $t_{1/2}$ is about 5 days at room temperature, that it does not have a large temperature coefficient, and that this is the exchange rate of the capping oxygen. Since there is a wide separation between the capping and bridging oxygen-exchange rates, the process by which the exchange takes place has to be much faster than any process that makes the two types of oxygen equivalent.

Table IX. Retention of Core Oxygens during Formation and Dissolution of Molybdenum(IV) Hydroxide[a]

no.	sample ($Mo_3O_4^{4+}$)	10^3R_N	^{18}O retention, %
1	standard	5.395	
	base treated	5.342	96
2	standard	5.124[b,c]	
	base treated	5.209[d]	100
	standard	5.241	
3	base treated	5.213[c]	98

[a] Enriched core oxygens; normal solvent. [b] Sample inadvertently contaminated with dust; enrichment diluted. [c] Room temperature. [d] 0 °C.

Exchange Rate: Bridging Oxygens, Type B. Table VIII gives the results of attempts to measure or at least set an upper limit to the exchange rate of the three bridging oxygens. Clearly some change is taking place over the long period investigated. Although the samples were kept under nitrogen, some oxidation to Mo(V) dimer occured (<30%) but this did not appear to markedly affect the rate. We did not find Mo(VI) present, but that would be unexpected since over the long times the Mo(VI)–Mo(IV) reaction would generate Mo(V). A similar study in 0.4 M HCl showed the same behavior, but the error was larger (only three points and t_{max} = 105 days). From the data, an estimated half-time of 5 ± 2 years is obtained and is not highly sensitive to acidity.

Oxygen Transfer through the Solid Hydroxide. A further demonstration of the kinetic stability of the $Mo_3O_4^{4+}$ core was made by following the ^{18}O retention upon conversion to the hydroxide precipitate followed by redissolving in acid. Table IX gives a representative experiment that shows that there is at least 98 ± 3% retention of the types A and B oxygens during the formation and solution of the hydroxide precipitate. These observations have considerable importance in the catalytic field because it demonstrates that the structure in solution can be and sometimes is transferred to the solid state. The hydroxide precipitate was candidate for use to sample the *waters* attached to the $Mo_3O_4^{4+}$ core. Several studies were initiated to ascertain its potential usefulness in this respect. In all cases, however, the oxygen of water held by the hydroxide precipitate had normalized with the solvent. Thus, the apparently rapid exchange occurring in the basic medium makes the hydroxide precipitate of little use for studying the coordinated waters. Since the types A and B oxygens remain during precipitation as the hydroxide, it was decided to "count" the total number of other oxygens in the dried precipitate by isotope dilution. This led to a range of values (12–23, average 19) that we were not able to stabilize and so made the OH^- precipitate not very useful for studing the core oxygens.

Kinetics of Water Exchange: Water, Type C. In order to measure the ^{18}O content of type C waters it was necessary to convert to a complex in which those waters are not replaced by ligands. From the structures of the SCN^- and ox^{2-} complexes it appeared that the three waters trans to the capping oxygen would be the least likely to be replaced by ligands and thus were the first whose kinetic behavior was studied. The oxalato complex, prepared in acidic media, has excellent properties for this type of study and when prepared rapidly has the same structure as previously reported.[6] We determined the structure of the $[Pt(en)_2]^{2+}$ salt to confirm that when prepared rapidly the coordinated waters were in the same position. The salt had the orthorhombic space group *Pbcn* and the formula $[Pt(en)_2][Mo_3O_4(ox)_3(OH_2)_3]\cdot 3H_2O$. Some of the waters of hydration can be removed by moderate heating under vacuum. Table X contains the important crystallographic data and structure solution description. The final conventional $R(F_o)$ is 3.6% with the inclusion of the hydrogen atoms with temperature factors of 5.0. Table XI gives the fractional atomic coordinates while Tables XII and XIII give selected bond distances and angles. The $[Pt(en)_2]^{2+}$ ions are square planar in the gauche configuration and have distances and angles nearly the same as in other compounds. Figure 2 gives a perspective drawing of the Mo complex ion, showing the placement of the coordinated waters. They are in equivalent positions trans to the capping (type A) oxygen at a bond distance of 2.161 (7) Å (average).

The exchange of type C waters was followed by monitoring the decrease in enrichment of the ion with time in a solvent of normal

Table X. Summary of the Data Collection Parameters Leading to the Structure of $[Pt(en)_2][Mo_3O_4(ox)_3(OH_2)_3]\cdot 3H_2O$

formula	$PtMo_3O_{22}N_4C_{10}H_{28}$
fw	1039.26
space gp	*Pbcn*
a, Å	9.115 ± 0.003
b, Å	17.840 ± 0.005
c, Å	34.040 ± 0.007
V, $Å^3$	5535.3 ± 4.5
Z	8
density, g/cm^3	calcd 2.494; obsd 2.480
cryst size, mm	approx 0.1 × 0.1 × 0.1
λ(Mo Kα), Å	0.710 73
monochromator	graphite
μ, cm^{-1}	15.2
abs cor: min; max	51%; 74%
scan method	θ-2θ step
scan range (θ), deg	$0.80 + 0.35 \tan\theta$
scan speed	variable to obtain 3% counting statistics to a max scan time of 120 s
no. of reflcns measd	4584
no. of indep reflcns	3575
no. of reflcns above 2σ	2847
no. of variables	372
$R(F_o) = \Sigma \lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert / \Sigma F_o$	0.036
$R_w(F_o) = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2 / \Sigma w F_o^2]^{1/2}$	0.045
max shift/error ratio on last cycle	0.08

enrichment. This approach was advantageous in that oxalate ion, used to complex the aquo ion, never came into contact with enriched solvent, and so its isotopic composition could be relied upon to be normal. This was a problem in the early experiments because oxalate ion undergoes relatively rapid oxygen exchange under mildly acidic conditions.

Figure 3 shows a typical $-\ln(1 - F)$ vs. time graph. All such graphs intercepted the *y* axis at the origin, indicating that there was no induced exchange upon complexation or precipitation of the ion, and the graphs were linear to about 6 half lives (the experimental limit of the method), proving only one exchange. On the basis of equilibrium times of $[Mo_3O_4(OH_2)_9]^{4+}$ with $H_2{}^{18}O$ and the rates of exchange, an average of 2.7 out of 3.0 type C waters on the ion should have exchanged. The average calculated from the R_N values at t_0 was 2.7 ± 0.2, indicating that there are 3.0 ± 0.2 oxygen atoms in the complex ion exchanging during the period of equilibration, a confirmation that we are looking at the correct exchanging species. Of course since the other six waters (type D) are replaced upon forming the complex, we have no information about their isotopic composition at this time. However, since they are fast to exchange, as shown later, the observation that only three oxygens turn up in the complex ion shows that substitution by oxalate ion takes place by Mo–O rupture. The rate constants for exchange, given in Table XIV, could be reproduced to ±2% and had a half-time of about 1 h at 25 °C in 1.0 M CH_3SO_3H. The reaction rate was not sensitive

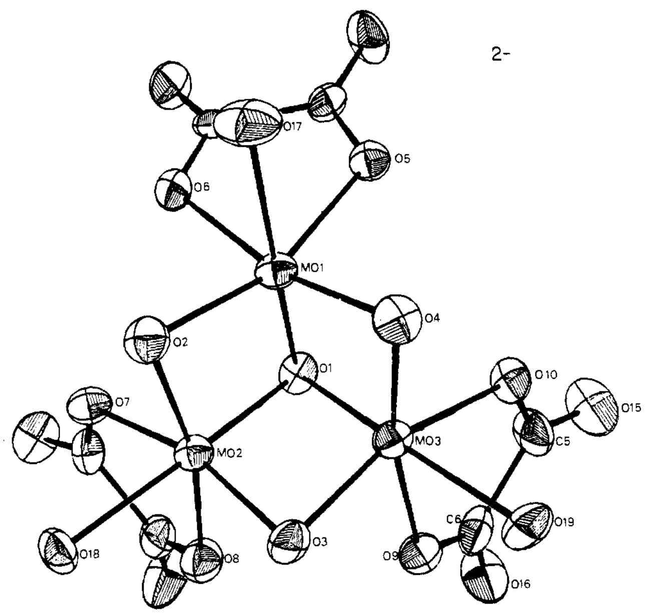

Figure 2. $[Mo_3O_4(C_2O_4)_3(OH_2)_3]^{2-}$.

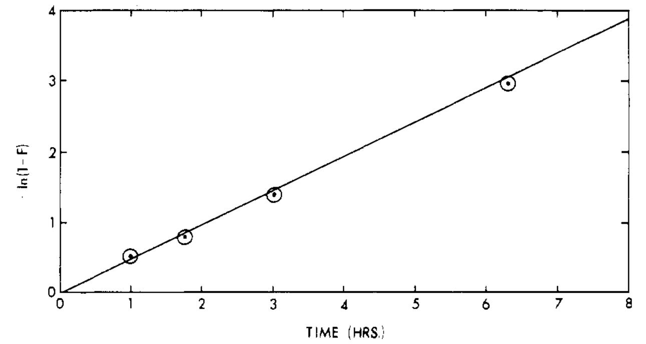

Figure 3. Rate of water exchange on $[Mo_3O_4(OH_2)_9]^{4+}$ (type C water; 25 °C).

Table XI. Atomic Coordinates of Atoms in the Unit Cell of $[Pt(en)_2][Mo_3O_4(ox)_3(OH_2)_3]\cdot 3H_2O$[a]

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Pt(1)	0.0000	0.00000	0.5000	O(17)	0.2160 (8)	0.1200 (4)	0.7594 (2)
Pt(2)	−0.5000	−0.10020 (3)	0.7500	O(18)	−0.1978 (8)	0.1244 (4)	0.6384 (2)
Mo(1)	0.2237 (1)	0.12286 (5)	0.69579 (3)	O(19)	0.2350 (10)	−0.0956 (4)	0.6437 (3)
Mo(2)	0.0395 (1)	0.12402 (5)	0.64149 (3)	O(W1)	0.3685 (11)	0.1358 (5)	0.4886 (3)
Mo(3)	0.2335 (1)	0.02532 (5)	0.64366 (3)	O(W2)	0.1245 (11)	0.1114 (5)	0.3986 (3)
O(1)	0.2592 (8)	0.1373 (4)	0.6377 (2)	O(W3)	−0.0768 (12)	0.3235 (6)	0.4325 (3)
O(2)	0.0140 (8)	0.1301 (4)	0.6975 (2)	O(W4)	0.1721 (13)	0.2667 (6)	0.3981 (4)
O(3)	0.0254 (8)	0.0176 (4)	0.6359 (2)	N(1)	0.010 (1)	0.1090 (5)	0.4818 (3)
O(4)	0.2437 (9)	0.0166 (4)	0.6997 (2)	N(2)	−0.212 (1)	0.0294 (6)	0.5142 (3)
O(5)	0.4488 (8)	0.1394 (4)	0.7043 (2)	N(3)	−0.381 (1)	−0.0253 (6)	0.7186 (3)
O(6)	0.2448 (9)	0.2392 (4)	0.7012 (2)	N(4)	−0.386 (1)	−0.1744 (5)	0.7167 (3)
O(7)	0.0203 (9)	0.2408 (4)	0.6393 (2)	C(1)	0.498 (1)	0.2053 (6)	0.7054 (3)
O(8)	0.0369 (8)	0.1496 (4)	0.5825 (2)	C(2)	0.377 (1)	0.2665 (6)	0.7006 (4)
O(9)	0.2854 (8)	0.0122 (4)	0.5846 (2)	C(3)	0.034 (1)	0.2735 (7)	0.6070 (4)
O(10)	0.4666 (8)	0.0157 (4)	0.6419 (2)	C(4)	0.035 (1)	0.2177 (7)	0.5720 (4)
O(11)	0.6250 (9)	0.2243 (5)	0.7122 (3)	C(5)	0.417 (1)	0.0028 (6)	0.5738 (3)
O(12)	0.4092 (11)	0.3332 (4)	0.6977 (3)	C(6)	0.528 (1)	0.0088 (6)	0.6081 (3)
O(13)	0.0482 (11)	0.3419 (4)	0.6010 (3)	C(7)	−0.141 (2)	0.1371 (7)	0.4773 (5)
O(14)	0.0375 (11)	0.2400 (5)	0.5381 (3)	C(8)	−0.229 (1)	0.1108 (7)	0.5119 (4)
O(15)	0.4605 (9)	−0.0099 (5)	0.5406 (2)	C(9)	−0.253 (2)	−0.0636 (7)	0.7023 (4)
O(16)	0.6607 (8)	0.0088 (4)	0.6024 (3)	C(10)	−0.306 (2)	−0.1353 (8)	0.6861 (4)

[a] Esd's given in parentheses.

Table XII. Bond Distances in $[Pt(en)_2][Mo_3O_4(C_2O_4)_3(OH_2)_3]\cdot 3H_2O$

atoms		dist, Å	atoms		dist, Å
Pt(1)	N(1)	2.043 ± 0.009	O(5)	C(1)	1.253 ± 0.013
Pt(1)	N(2)	2.055 ± 0.010	O(6)	C(2)	1.299 ± 0.014
Pt(2)	N(3)	2.027 ± 0.009	O(7)	C(3)	1.254 ± 0.014
Pt(2)	N(4)	2.027 ± 0.010	O(8)	C(4)	1.268 ± 0.013
Mo(1)	Mo(2)	2.497 ± 0.001	O(9)	C(5)	1.266 ± 0.013
Mo(1)	Mo(3)	2.487 ± 0.001	O(10)	C(6)	1.284 ± 0.013
Mo(1)	O(1)	2.019 ± 0.007	O(11)	C(1)	1.234 ± 0.013
Mo(1)	O(2)	1.912 ± 0.007	O(12)	C(2)	1.229 ± 0.014
Mo(1)	O(4)	1.907 ± 0.007	O(13)	C(3)	1.242 ± 0.013
Mo(1)	O(5)	2.093 ± 0.008	O(14)	C(4)	1.221 ± 0.014
Mo(1)	O(6)	2.093 ± 0.008	O(15)	C(5)	1.220 ± 0.013
Mo(1)	O(17)	2.165 ± 0.007	O(16)	C(6)	1.217 ± 0.012
Mo(2)	Mo(3)	2.497 ± 0.001	N(1)	C(7)	1.484 ± 0.016
Mo(2)	O(1)	2.018 ± 0.007	N(2)	C(8)	1.462 ± 0.015
Mo(2)	O(2)	1.922 ± 0.008	N(3)	C(9)	1.462 ± 0.017
Mo(2)	O(3)	1.912 ± 0.007	N(4)	C(10)	1.453 ± 0.016
Mo(2)	O(7)	2.090 ± 0.007	C(1)	C(2)	1.558 ± 0.016
Mo(2)	O(8)	2.059 ± 0.007	C(3)	C(4)	1.551 ± 0.017
Mo(2)	O(18)	2.161 ± 0.007	C(5)	C(6)	1.553 ± 0.016
Mo(3)	O(1)	2.023 ± 0.007	C(7)	C(8)	1.494 ± 0.020
Mo(3)	O(3)	1.921 ± 0.007	C(5)	O(15)	1.220 ± 0.013
Mo(3)	O(4)	1.914 ± 0.007	C(6)	O(16)	1.217 ± 0.012
Mo(3)	O(10)	2.133 ± 0.007			
Mo(3)	O(19)	2.157 ± 0.007			

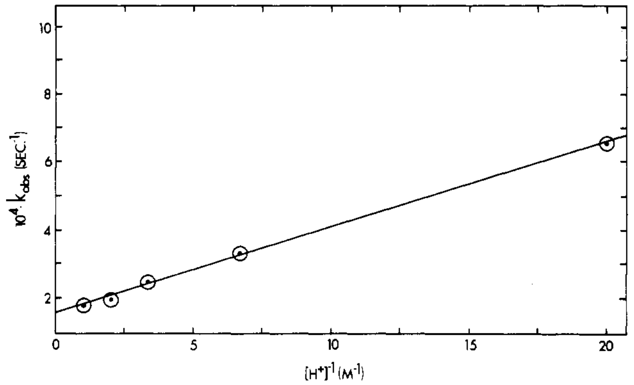

Figure 4. Water-exchange rate constants (k_{obsd} vs. $1/[H^+]$ (type C waters); 25 °C).

to light, was independent of $[Mo_3O_4]^{4+}$, increased slightly with increasing ionic strength both in CH_3SO_3H and in HCl media, was not significantly altered by 10^{-5} M $Mo_2O_4^{2+}$ or 2×10^{-4} M MoO_4^{2-}, but appeared to decrease when $Mo_3O_4^{4+}$(aq) was complexed with the stoichiometric amount of oxalate ion (note however that the acidity also changed in that run). The effect of acidity is shown in Figure 4 where the rate decreases with increasing acid concentration at constant I. Noting the linear behavior and intercept, the interpretation is that $k_{obsd} = k_0 + k_{OH}/[H^+]$ where k_0 is for the aquo ion, k_{OH} is for the first hydrolysis product

$$[Mo_3O_4(OH_2)_9]^{4+} \rightleftharpoons [Mo_3O_4(OH_2)_8(OH)]^{3+} + H^+$$

and $k_{obsd} = k_0 + k_{OH}K_a[H^+]^{-1}$.

A nonweighted least-squares analysis gave $k_0 = (1.54 \pm 0.11) \times 10^{-4}$ s^{-1} and $K_ak_{OH} = (2.24 \pm 0.06) \times 10^{-4}$ M s^{-1} at 25 °C and $I = 1.00$. A rough estimate was made of K_a by pH measurement of a freshly prepared solution of the oxalate complex. Assuming no ox^{2-} dissociation and that the acid dissociation constant is not changed by the coordination of ox^{2-}, one gets a value of about 10^{-4} M. The other six waters coordinated in the aquo ion are less tightly bound, Mo–O distance 2.26 Å compared to 2.16 Å for the SCN^- and ox^{2-} complexes, respectively, and thus would be less acidic. A reasonable estimate for K_a for them would be 10^{-6} M. Since it is unlikely that deprotonation of the water being exchanged would facilitate exchange and since the effect of hydrolysis on one Mo would not be felt on another Mo of the cluster, it is likely that the hydrolysis of the type D water is responsible for the enhanced lability of the type C waters. So, k_{OH} is estimated to be about 25 s^{-1}. Such a large change upon hydrolysis is consistent with previous observations.[11]

The activation parameters were estimated at $[H^+] = 1.00$ and 0.05M. It was estimated that in 1.00 M acid 88% of the exchange is carried by the k_0 term while at 0.05 M that value is 24%. A weighted evaluation of ln k_{obsd} vs. $1/T$ for 0, 15, and 25 °C data for each acid gave good linear fits and, assuming the transmission coefficients to be unity, gave the following: 1.0 M H^+, $\Delta H^* = 104.9 \pm 0.4$ kJ mol^{-1} and $\Delta S^* = 37.2 \pm 1.5$ J mol^{-1} K^{-1}; at 0.05 H^+, $\Delta H^* = 100.4 \pm 1.7$ kJ mol^{-1} and $\Delta S^* = 28 \pm 6$ J mol^{-1} K^{-1}. Within experimental error these values are identical. The high positive ΔS^* values suggest appreciable dissociative character leading to the activated state.

The rate of water exchange on the tris(oxalato) complex of Mo(IV) was measured at low acidity because the carboxylate ligands are easily removed at higher acidities, especially in the absence of excess ligand. The number of waters exchanging, counted by isotope dilution, was found to be 3.0 ± 0.1. Since the formation constants are not known, the fraction of ox^{2-} free at equilibrium cannot be calculated at any pH, but on the basis of its ion-exchange properties and its precipitation behavior in the presence of Pb^{2+} the amount of free ox^{2-} at pH 3.5 is less than 5% of the total.

Chloride ion weakly associates with aquo molybdenum(IV), and it was of interest to determine its effect on the rate of water exchange of type C waters. It has been shown[16] that Mo(IV), equilibrated with 4 M HCl, produces three chloro complexes with the ion-exchange behavior expected for $[Mo_3O_4(OH_2)_8Cl]^{3+}$, $[Mo_3O_4(OH_2)_7Cl_2]^{2+}$, and $[Mo_3O_4(OH_2)_6Cl_3]^+$ in addition to the aquo ions. These ions were separated at 0 °C on an ion-exchange resin and the equilibrium constants determined by measuring the amounts of each spectrally after conversion to the aquo ion. They had the values $K_1 = 0.47$ M^{-1}, $K_2 = 0.27$ M^{-1}, and $K_3 = 0.07$ M^{-1} at 25 °C. The $t_{1/2}$'s for aquation of these chloro complexes were nearly the same, about 20 min at 0 °C, determined by a spectral ion-exchange method.

For the oxygen-exchange runs in Cl^- medium it was necessary to show that the precipitated oxalate complex did not contain Cl^-. This was demonstrated by two experiments: (a) treating the dissolved complex with acidic Ag^+ (no precipitate); (b) following the absorbance of the supernatant solution from the precipitation of the oxalate complex as a function of time of contact of Mo(IV) with HCl under the conditions of the exchange runs. (The chloro complexes are not precipitated under these circumstances.) In 3 h there was essentially no change in the absorbance of the sample supernate, but after 20 or 40 h the absorbance changed, proving that significant amounts of chloro complexes form in 20 h. The maximum time of the water-exchange experiments was 2.0 h so no appreciable complexation by Cl^- occurred at the C position. However, substitution at the D positions is much faster, and during the formation of the oxalate species, Cl^- in those positions would be replaced. Thus, Cl^- is probably partially occupying the D positions during the ^{18}O exchange on the C water positions but is replaced by oxalate ion when the Mo(IV) is collected on a resin, washed, and complexed with ox^{2-}. The rate constants for water exchange of type C Mo(IV) waters are smaller in the presence of Cl^- as shown in Table XIV at constant ionic strength, but the effect is small and comparison shows the ionic strength has a larger (and in the opposite direction) effect.

Water-Exchange Rates (Type D Waters). Four runs were made in an attempt to quantitatively measure this exchange rate. The first two established a holdback of oxygen at t_0 by $[Mo_3O_4(OH_2)_9]^{4+}$ to an extent greater than seven oxygens (types A–C), and appreciable exchange occurs in 10–15 min at 0 °C. This

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Table XIII. Selected Bond Angles in $[Pt(en)_2][Mo_3O_4(C_2O_4)_3(OH_2)_3]\cdot 3H_2O$

atoms			angle, deg	atoms			angle, deg
N(1)	Pt(1)	N(2)	82.67 ± 0.41	O(1)	Mo(2)	O(18)	170.52 ± 0.29
Mo(2)	Mo(1)	Mo(3)	60.12 ± 0.04	O(2)	Mo(2)	O(3)	98.39 ± 0.32
Mo(2)	Mo(1)	O(1)	51.76 ± 0.20	O(2)	Mo(2)	O(7)	88.27 ± 0.32
Mo(2)	Mo(1)	O(2)	49.52 ± 0.24	O(2)	Mo(2)	O(8)	162.43 ± 0.29
Mo(2)	Mo(1)	O(4)	97.09 ± 0.23	O(2)	Mo(2)	O(18)	85.96 ± 0.30
Mo(2)	Mo(1)	O(5)	139.51 ± 0.22	O(3)	Mo(2)	O(7)	168.43 ± 0.30
Mo(2)	Mo(1)	O(6)	96.82 ± 0.22	O(3)	Mo(2)	O(8)	96.98 ± 0.30
Mo(2)	Mo(1)	O(17)	135.93 ± 0.20	O(3)	Mo(2)	O(18)	86.02 ± 0.29
Mo(3)	Mo(1)	O(1)	52.09 ± 0.20	O(7)	Mo(2)	O(8)	75.21 ± 0.30
Mo(3)	Mo(1)	O(2)	95.98 ± 0.23	O(7)	Mo(2)	O(18)	85.02 ± 0.30
Mo(3)	Mo(1)	O(4)	49.52 ± 0.22	O(8)	Mo(2)	O(18)	86.67 ± 0.30
Mo(3)	Mo(1)	O(5)	99.39 ± 0.20	Mo(1)	Mo(3)	Mo(2)	60.14 ± 0.04
Mo(3)	Mo(1)	O(6)	138.86 ± 0.23	Mo(1)	Mo(3)	O(1)	51.96 ± 0.20
Mo(3)	Mo(1)	O(17)	134.29 ± 0.21	Mo(1)	Mo(3)	O(3)	96.44 ± 0.22
O(1)	Mo(1)	O(2)	100.29 ± 0.31	Mo(1)	Mo(3)	O(4)	49.28 ± 0.22
O(1)	Mo(1)	O(4)	100.35 ± 0.29	Mo(1)	Mo(3)	O(9)	140.99 ± 0.20
O(1)	Mo(1)	O(5)	87.82 ± 0.29	Mo(1)	Mo(3)	O(10)	96.48 ± 0.21
O(1)	Mo(1)	O(6)	86.78 ± 0.30	Mo(1)	Mo(3)	O(19)	134.40 ± 0.24
O(1)	Mo(1)	O(17)	170.45 ± 0.29	Mo(2)	Mo(3)	O(1)	51.75 ± 0.20
O(2)	Mo(1)	O(4)	99.22 ± 0.31	Mo(2)	Mo(3)	O(3)	49.20 ± 0.20
O(2)	Mo(1)	O(5)	164.52 ± 0.29	Mo(2)	Mo(3)	O(4)	96.92 ± 0.22
O(2)	Mo(1)	O(6)	91.30 ± 0.31	Mo(2)	Mo(3)	O(9)	102.23 ± 0.20
O(2)	Mo(1)	O(17)	86.58 ± 0.31	Mo(2)	Mo(3)	O(10)	139.61 ± 0.21
O(4)	Mo(1)	O(5)	92.18 ± 0.30	Mo(2)	Mo(3)	O(19)	135.16 ± 0.24
O(4)	Mo(1)	O(6)	165.96 ± 0.31	O(1)	Mo(3)	O(3)	99.77 ± 0.29
O(4)	Mo(1)	O(17)	84.94 ± 0.30	O(1)	Mo(3)	O(4)	99.99 ± 0.30
O(5)	Mo(1)	O(6)	75.89 ± 0.30	O(1)	Mo(3)	O(9)	89.34 ± 0.28
O(5)	Mo(1)	O(17)	84.01 ± 0.29	O(1)	Mo(3)	O(10)	87.87 ± 0.29
O(6)	Mo(1)	O(17)	86.44 ± 0.30	O(1)	Mo(3)	O(19)	171.04 ± 0.30
Mo(1)	Mo(2)	Mo(3)	59.73 ± 0.04	O(3)	Mo(3)	O(4)	100.28 ± 0.32
Mo(1)	Mo(2)	O(1)	51.81 ± 0.20	O(3)	Mo(3)	O(9)	94.83 ± 0.31
Mo(1)	Mo(2)	O(2)	49.17 ± 0.20	O(3)	Mo(3)	O(10)	167.07 ± 0.30
Mo(1)	Mo(2)	O(3)	96.35 ± 0.22	O(3)	Mo(3)	O(19)	86.21 ± 0.32
Mo(1)	Mo(2)	O(7)	95.16 ± 0.22	O(4)	Mo(3)	O(9)	160.55 ± 0.30
Mo(1)	Mo(2)	O(8)	135.94 ± 0.21	O(4)	Mo(3)	O(10)	88.52 ± 0.31
Mo(1)	Mo(2)	O(18)	135.02 ± 0.23	O(4)	Mo(3)	O(19)	85.36 ± 0.32
Mo(3)	Mo(2)	O(1)	51.92 ± 0.20	O(9)	Mo(3)	O(10)	74.71 ± 0.29
Mo(3)	Mo(2)	O(2)	95.40 ± 0.21	O(9)	Mo(3)	O(19)	83.49 ± 0.30
Mo(3)	Mo(2)	O(3)	49.52 ± 0.21	O(10)	Mo(3)	O(19)	85.07 ± 0.32
Mo(3)	Mo(2)	O(7)	139.61 ± 0.22	Mo(1)	O(1)	Mo(2)	76.43 ± 0.25
Mo(3)	Mo(2)	O(8)	101.04 ± 0.21	Mo(1)	O(1)	Mo(3)	75.95 ± 0.25
Mo(3)	Mo(2)	O(18)	135.33 ± 0.21	Mo(2)	O(1)	Mo(3)	76.33 ± 0.25
O(1)	Mo(2)	O(2)	100.00 ± 0.29	Mo(1)	O(2)	Mo(2)	81.30 ± 0.29
O(1)	Mo(2)	O(3)	100.27 ± 0.29	Mo(2)	O(3)	Mo(3)	81.28 ± 0.25
O(1)	Mo(2)	O(7)	87.79 ± 0.29	Mo(1)	O(4)	Mo(3)	81.20 ± 0.28
O(1)	Mo(2)	O(8)	85.53 ± 0.29	Mo(3)	O(10)	C(6)	118.26 ± 0.67

exchange could not come from either the core oxygens or the type C water oxygens because of their much slower rate at this temperature. The time zero values however were greater than 4 × 10^{-3} because the precipitate contained an unknown (and partially variable) number of waters of hydration. Attempts at removing this hydrated water under vacuum resulted in some exchange between the type D waters and the waters of hydration. Thus, drying of the precipitate was restricted to surface water. The third run gave a rough value for the half-time, about 30 min at 0 °C, but there was considerable question about the infinite value and thus about k since the exchange was only followed for about 1 half-time. The final set of data consisted of eight points and a careful solvent value. The data followed first-order kinetics and $k_{obsd} = (4.9 \pm 1.0) \times 10^{-4}$ s^{-1} at 0 °C in 1.2 M acid, $t_{1/2} = 24 \pm 5$ min. The method is not very satisfying and not likely to be significantly improved upon, but we feel that this at least establishes the magnitude of this water-exchange rate.

Oxygen Transfer upon Reduction of $Mo_3O_4^{4+}$(aq). The proposed trimeric structures for the reduction products of $Mo_3O_4^{4+}$(aq) in noncomplexing media were based primarily upon the reversible nature of the reduction and the fact that the reduced species could be electrolytically or chemically reoxidized to trimer Mo(IV).[9,10] However, no conclusive evidence discounting the possibility of the trimeric structure opening and re-forming was presented. Table XV shows the results of our experiments designed to answer the question to what extent are the four core oxygens retained in forming the reduced species and reoxidizing it back to the starting ion. All oxygen atom transfer experiments in which $Mo_3O_4^{4+}$(aq) was reduced to $Mo^{III}{}_3$ or $Mo^{III}{}_2Mo^{IV}$ and reoxidized with O_2 to $Mo_3O_4^{4+}$(aq) (determined spectrally) showed core-oxygen retentions of 93% or greater. On the basis of these results we conclude that the trimeric nature of the reduced species, reported by Sykes,[9] has been confirmed. An experiment where ^{18}O-enriched $Mo^{III}{}_3$ was allowed to sit in normal water under N_2 at room temperature for approximately 2 months showed that, within experimental error, there was no loss of enrichment in any of the oxygens of the core. Thus, reduction produces a species that is even more inert to substitution at the core positions than the starting ions ($t_{1/2}$ capping oxygen of $Mo_3O_4^{4+}$(aq) = 5 days). These conclusions limit the structural possibilities for the reduced species.

Discussion

Experiments showing essentially complete retention of four oxygens per trimer of Mo(IV) in two complexes of known solid-state structure, obtained by rapid complexation of the aquo ion in a solvent of differing isotopic oxygen composition, clearly demonstrate that $Mo_3O_4^{4+}$(aq) is the kinetically stable species in acid media. The ability to transform one complex into another and even into an insoluble hydroxide without core-oxygen exchange establishes that the $Mo_3O_4^{4+}$ core is stable kinetically and under a variety of reactive conditions. No evidence has been presented for the existence of monomeric species in aqueous solution, except as a transient, even in very dilute acidic solutions, and thus it

Table XIV. Rates of Solvent Exchange with Type C Waters of $Mo_3O_4^{4+}(aq)$

$[Mo_3O_4^{4+}]$, M	$[H^+]$, M	I,[a] M	temp, °C	special conditions	$t_{1/2}$, h	$10^5 k_{obsd}$, s^{-1}
0.0195	1.00	1.00	25.0		1.10	17.47 ± 0.24
0.0195	1.00	1.00	25.0		1.14	16.95 ± 0.17
0.0094	1.00	1.00	25.0		1.14	16.85 ± 0.36
0.0025	1.00	1.00	25.0		1.07	17.95 ± 0.64
0.0195	1.00	1.00	25.0	no light	1.13	17.02 ± 0.39
0.0098	0.50	1.00	25.0		1.01	19.12 ± 0.19
0.0059	0.30	1.00	25.0		0.78	24.79 ± 0.32
0.0029	0.15	1.00	25.0		0.58	32.93 ± 0.36
0.00098	0.05	1.00	25.0		0.30	64.88 ± 0.50
0.0195	1.00	1.00	0.0		45.2	0.426 ± 0.002
0.0195	1.00	1.00	15.0		4.70	4.10 ± 0.52
0.0098	0.05	1.00	0.0		7.00	2.75 ± 0.16
0.0098	0.05	1.00	15.0		2.03	9.47 ± 1.03
0.015	1.00	2.00	25.0		0.91	21.1 ± 0.3
0.010	0.50	0.50	25.0		1.04	18.6 ± 1.5
0.0195	1.00	1.00	25.0	1 M Cl^-	1.45	13.30 ± 0.22
0.0150	1.00	2.00	25.0	2 M Cl^-	1.26	15.28 ± 0.27
0.0195	1.00	1.00	25.0	10^{-5} M $Mo_2O_4^{2+}$	1.21	15.9 ± 0.2
0.0195	1.00	1.00	25.0	2×10^{-4}M MoO_4^{2-}	1.19	16.2 ± 0.6
0.020[b]	3.16×10^{-4}	1.00	25.0	no free ox^{2-}	0.79	24.3 ± 2.1
0.02[b,c]	1×10^{-4}	1.0	15.0	free ox^{2-}	3.67	15.2 ± 0.1
0.02[b,c]	1×10^{-4}	1.0	25.0	free ox^{2-}	0.75	25.7 ± 0.5
0.02[b,c]	1×10^{-4}	1.0	25.0	free ox^{2-}	0.67	28.7 ± 0.5
0.02[b,c]	1×10^{-4}	1.0	25.0	no free ox^{2-}	0.75	25.7 ± 0.5

[a] CH_3SO_3H-$CH_3SO_3^-$. [b] Exchange measurement on oxalate complex. [c] Exchange measurement on oxalate complex. Samples precipitate with 1:1 CH_3CN-H_2O solution.

Table XV. ^{18}O Retention after Reduction and Reoxidation $Mo^{IV}{}_3 \rightarrow Mo^{III}{}_3 \rightarrow Mo^{IV}{}_3$

reduced state[a,b]	sample	$10^3 R_N$	^{18}O retention, %
$Mo^{III}{}_2Mo^{IV}$	reduced[e]	5.632 (1)	93.4
	unreduced[e]	5.744 (1)	
$Mo^{III}{}_3$	reduced	5.558 (1)	96.9
	unreduced	5.606 (1)	
$Mo^{III}{}_3$	reduced	5.304 (1)	97.1
	unreduced	5.342 (1)	
$Mo^{III}{}_3$	reduced	5.304, 5.403, 5.460[c]	
	unreduced	5.342 (1)	

[a] The infinity value for complete exchange was 4.06×10^{-3}. [b] 1.0 M H^+. [c] These values are for exchange times of 0, 8 days, and 2 months, respectively. The slight increase is due to instrumental changes over the long period of time. [d] Reductions and oxidations carried out at ambient temperature. [e] In all cases, the oxygen content of $[Pt(en)_3][Mo_3O_4(ox)_3(OH_2)_3]_2 \cdot 3H_2O$ was measured.

appears that the strong (2.493 (3) Å) Mo–Mo bond, coupled with the effect of bridging oxygens, effectively dominates the aqueous chemistry of Mo(IV).

While rates of solvent exchange are not necessarily related to solid-state bond distances, it seems, intuitively, that a casual relationship should exist. This study gives the first case in which four differing oxygens on a metal ion have been counted and identified as to their position and rate of isotopic exchange and the rates of isotopic exchange compared with the respective M–O distances. All bonds appear to be in the single-bond range, and thus the mechanistic changes expected with M=O bonds are not present. In acidic media the following approximate comparison can be made:

oxygen type	protons	Mo–O (av), Å	approx $t_{1/2}$(ex),[a] s (temp, °C)
A	0	2.020 (3)	1×10^5 (0)
B	0	1.916 (7)	2×10^8 (22)
C	2	2.163 (3)	2×10^5 (0)
D	2	2.26 (2)[b]	1×10^3 (0)

[a] 1 M H^+. [b] This value comes from the SCN^- complex structure.

There appears to be a significant inverse relationship between the single-bond distance and the water-exchange rate. Only type C oxygen appears to have a major inverse acidity rate term, but the bond distance–exchange rate relationship is still complete, even using the k_0 term for that water. Whether this bond distance–exchange rate connection is a general phenomenon remains to be seen, but there is an obvious recent case where it is not followed. For $Mo_2O_4^{2+}$ both the -yl and bridging oxygens have been studied and the former is considerably faster to exchange than the bridging oxygen ($t_{1/2} = 2 \times 10^2$, $>5 \times 10^6$ s at 0 °C, respectively) although the bond distances are 1.70 (3) and 1.90 (3) Å, respectively.[12] Mechanistic factors play the most important role here.

Related to this is the connection between M–O bond distances for oxygens trans to each other. As one bond shortens, the bond trans to it lengthens, suggesting that the sum of the two bonds ought to be a constant. That appears to be the case (types A + C = 4.183 Å; types B + D = 4.176 Å). This may be another example of the previous observation that the octahedron of ligands tends to be conserved and it is the metal ion that moves in distorted structures (see $MoOCl_4OH_2^-$ [13]).

This study reveals the natural slowness of bridging oxygens (types A and B) to exchange with solvent, also found with Mo(V) complexes.[14] The fact that the capping oxygen is much faster to exchange than the bridging oxygens suggests that its exchange occurs predominantly through the breaking of one or two of its Mo–O bonds and that the main path does not involve a complete separation of two Mo atoms through breaking of both types A and B bonds. Otherwise, exchange would occur for both kinds of oxygen at similar rates.

An attractive mechanism for μ_3-oxygen exchange involves water approach from the opposite face of the Mo_3 triangle, giving, reversibly, a symmetrial bicapped complex and exchange. Such bicapped complexes have been shown to exist.[18]

For d^2 ions of this high oxidation state one generally predicts much faster water rates of exchange than were found. In this case the metal–metal interaction most likely renders associative interactions energetically unfavorable. A more likely mechanism would be one predominately dissociative in nature. One possible explanation is that the metal-to-metal bond order increases at the transition state to electronically stabilize a dissociated activated complex. Similar reversible changes in bond order have been found to parallel decreases in coordination number in some multiply bound molybdenum dimers.[15] The fact that the rate constants

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for exchange parallel their respective Mo–O bond distances is also suggestive of a primarily dissociative type mechanism. Also, counting the metal–metal bonds, each molybdenum has a coordination number of 8, making it a crowded site for an associative mechanism.

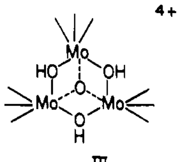
There appears to be an inconsistency between this solvent-exchange study and a study of the rate of SCN^- association with Mo(IV). The data show that SCN^- substitution (presumably at the type D positions) is much faster than water exchange even at the D positions.[2] Furthermore, coordination of oxalate ion or SCN^- at the D positions slows down the rate of exchange of the remaining waters. These observations are not inconsistent, however, and can be explained simply. Ion-pair formation between $Mo_3O_4^{4+}$ and these negative ligands would be extensive. The effect of ion-pair formation on the rate of water exchange of D waters would be to enhance it since the ion charge is effectively lowered and the water dipole would be more weakly attracted to the metal ion. Rates of anation are, as a rule, governed by the respective water-exchange rate. Thus, the anation rate would appear faster in complexing medium than the corresponding rate of water exchange in noncomplexing medium. In the presence of the ligands at equilibrium, however, they are largely coordinated at the D positions and the observed water-exchange rate is close to that of the slower C position oxygens.

The three waters coordinated in C positions, opposite the capping oxygen, were capable of being studied in reasonable detail. The rate was not much affected by light, $[Mo_3O_4]^{4+}$, ionic strength, $[Cl^-]$, or small amounts of Mo(V) or Mo(VI). The rate constant was dramatically increased in the less acidic region and could be analyzed through the k_0 and k_{OH} terms. The latter was estimated to be 25 s^{-1}, about 10^6 greater than k_0. When the D positions of $Mo_3O_4^{4+}$ are complexed by ox^{2-} (tris(oxalato) complex), the C waters could be studied but not in very acidic solution because the ligand dissociates from the complex and it also exchanges with the solvent. The number of exchanging oxygens when counted amounted to three, and the rate is considerably slower than that measured for the aquo ion. This probably resulted from the impossibility of having an I_d conjugate base mechanism in the oxalato complex and no k_{OH} term. A comparison of the k_0 terms should show them to be nearly the same, assuming the charge effect to be small. The values 1.5×10^{-4} and 2.0×10^{-4} s^{-1}, respectively, are sufficiently close to suggest that with ox^{2-} occupying the D positions only the k_0 term for oxygen exchange remains and that it is not changed significantly when ox^{2-} is in the coordination sphere. A study of the effect of Cl^- coordinated in the D positions on the ^{18}O rate of exchange on the C type waters is difficult because one cannot fill the D positions with Cl^- even at the highest $[Cl^-]$ possible. However, in 1 and 2 M HCl where appreciable coordination takes place the rate of O exchange of C type waters decreased only slightly. Our explanation of the Cl^- effect lies in having Cl^- partially filling the D positions and thereby lowering the probability of hydrolysis of the D water, both by reducing their number and by lowering the positive charge on the ion and thereby lowering the k_{OH} term. Thus, we come to the conclusion that C type waters exchange relatively independent of the aqueous environment and of the ligands in the D positions.

Little can be said of the activation parameters for the aquo ion except to point out that both $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are in the correct range for a primarily dissociative process.

Measurement of the exchange rates on the D type waters was very difficult and in our hands imprecise. No really suitable precipitating agent was found. However, using $[Mo(CN)_8]^{4-}$ under very specific conditions, we were able to show that the rate was measurable by our techniques at 0 °C in acidic media and not nearly as fast as the SCN^- or ox^{2-} coordination at these positions. Thus, we suggest that the rate of exchange of type D waters is very sensitive to its aqueous environment including ion-pairing effects.

Armed with the knowledge of the slowness of the types A and B oxygens allows definitive studies on oxygen transfer during certain oxidation–reduction reactions. Oxidation of Mo^{IV}_3 appears always to be irreversible, but reduction has been shown to be reversible under a wide variety of conditions. The experiments show conclusively that all of the core oxygens of $Mo_3O_4^{4+}$(aq) are retained when it is electronically reduced to either Mo^{III}_3 or $Mo^{III}_2Mo^{IV}$ and reoxidized to the starting material. Furthermore, whatever the structure of Mo^{III}_3 or $Mo^{III}_2Mo^{IV}$ all four oxygens exchange in acid solution much more slowly than the capping oxygen of $Mo_3O_4^{4+}$(aq). The structures proposed[9,10] all involve protonation of the oxo groups to retain a high positive charge suggested by ion-exchange behavior. In our opinion it is unlikely that protonation of the capping oxygen occurs with the result of breaking one or more of its bonds to Mo because this would result in exchange unless the oxygen remained doubly bonded. It is more likely that the protonation occurs on the bridging oxygen (type B) and is reversible upon oxidation. Thus, the maximum number of protons added would be three and the ion would have the formula



Mo^{III}_3

Since this is a d^3 ion for the completely reduced state, it would (by analogy with Cr(III)) be quite inert to substitution.

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Registry No. O_2, 7782-44-7; $[Mo_3O_4(H_2O)_9]^{4+}$, 74353-85-8; $[Pt(en)_2][Mo_3O_4(ox)_3(OH_2)_3]\cdot 3H_2O$, 95585-74-3; H_2O, 7732-18-5; $[Mo_3O_4(H_2O)_9]^+$, 95464-88-3; $[Mo_3O_4(ox)_3(H_2O)_3]^{2-}$, 85165-05-5; $[Mo_3O_4(NCS)_9]^{5-}$, 74358-60-4; $[Co(en)_3][Mo_3O_4(ox)_3(OH_2)_3]Hox$, 95586-04-2; $[Pt(en)_3][Mo_3O_4(ox)_3(OH_2)_3](Hox)_2$, 95586-05-3; $[(CH_3)_4N]_4[Mo_3O_4(NCS)_8(OH_2)]$, 82428-66-8; $[(CH_3)_4N]_5[Mo_3O_4(NCS)_9]$, 74358-61-5.

Supplementary Material Available: Listings of observed and calculated structure factors, rms amplitudes, and temperature factor expressions (37 pages). Ordering information is given on any current masthead page.