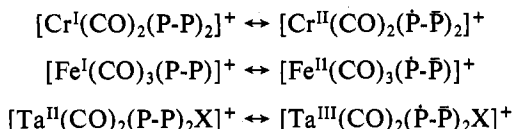plexes in this work, the group 6 17-electron cations, [M-(CO)₂(P-P)₂]⁺, are sufficiently stable that ESR data can be obtained. A substantial ³¹P hyperfine interaction is observed in all cases. For example, [Cr(CO)₂(P-P)₂]⁺ complexes give simple five-line spectra. Similarly, [Fe(CO)₃(P-P)]⁺ species exhibit three-line spectra because of coupling with two equivalent phosphorus atoms.[3]

The data above suggest that bidentate phosphorus ligands have a remarkable ability to stabilize 17-electron systems in formally, unusual oxidation states. It is likely that this property arises from substantial delocalization of the unpaired electron onto the phosphorus atoms. That is, a stabilized species can be formed by transfer of an electron from the metal d levels to the phosphorus orbitals, leaving the metal in a common, stable oxidation state. For example

$$[Cr^I(CO)_2(P\text{-}P)_2]^+ \leftrightarrow [Cr^{II}(CO)_2(\dot{P}\text{-}\bar{P})_2]^+$$

$$[Fe^I(CO)_3(P\text{-}P)]^+ \leftrightarrow [Fe^{II}(CO)_3(\dot{P}\text{-}\bar{P})]^+$$

$$[Ta^{II}(CO)_2(P\text{-}P)_2X]^+ \leftrightarrow [Ta^{III}(CO)_2(\dot{P}\text{-}\bar{P})_2X]^+$$

where (Ṗ-P̄) is a delocalized electronic configuration. These resonance structures are equivalent to an internal disproportionation; 17-electron systems commonly disproportionate in the usual sense to produce more stable configurations.[37–39] The ¹⁸¹Ta and ³¹P hyperfine interactions observed in the ESR spectrum of [(η-C₅H₄Me)₂Ta(DMPE)][BF₄]₂ are consistent with this hypothesis; i.e., the Ta(V) resonance form makes an important contribution. Thus, $a_{^{181}Ta}$ (42 G) is

$$[(\eta\text{-}C_5H_4Me)_2Ta^{IV}(P\text{-}P)]^{2+} \leftrightarrow [(\eta\text{-}C_5H_4Me)_2Ta^V(\dot{P}\text{-}\bar{P})]^{2+}$$
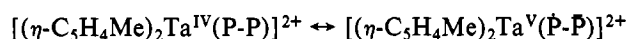
substantially smaller than for (η-C₅H₄Me)₂TaMe₂ (93 G),[22] where the odd electron is, presumably, located principally on tantalum. Similarly, $a_{^{31}P}$ (29 G) is large.

The possibility of forming phosphorus anion radicals with bidentate ligands appears to be considerable, since electrochemical studies on triphenylphosphine and triphenylphosphine oxide demonstrate that their anion radicals can be produced

via electrochemical reduction in aprotic solvents.[40] With the oxide, reduction in ethers with alkali metals produces an ESR signal characteristic of the reported species. Additional stabilization could be expected for bidentate ligands, but no data appear to be available.

Finally, in situations where one-electron oxidation produces 17-electron systems in formally common, stable, oxidation states, stable species can be formed without transfer of electron density to phosphorus. For example, the ³¹P hyperfine in the ESR spectrum of [Mn^{II}(CO)₃(P-P)X]⁺ is small and unresolved. However, the splitting arising from the metal hyperfine interaction is substantial.[10]

In summary, it can be concluded that the ability of bidentate phosphorus ligands to promote the oxidation of organometallic species to 17-electron systems in, formally, unusual oxidation states is widespread. This work establishes that this ability is not a feature of a particular metal or geometry. Stabilization may be attributable to the occurrence of an internal disproportionation, delocalizing electron density into the phosphorus orbitals, leaving the metal in a more common oxidation state.

Registry No. [(η-C₅H₄Me)₂Ta(DMPE)][BF₄], 73286-12-1; [(η-C₅H₄Me)₂Ta(DMPE)]Br, 73274-59-6; [(η-C₅H₄Me)₂Ta-(DMPE)][BF₄]₂, 73274-61-0; Ta(CO)₂(DMPE)₂Cl, 61916-36-7; Ta(CO)₂(DMPE)₂Br, 61966-89-0; Ta(CO)₂(DMPE)₂I, 65015-81-8; Ta(CO)₂(DMPE)₂CH₃, 61916-24-3; Ta(CO)₂(DMPE)₂H, 50600-13-0; Ta(CO)₂(DMDEPE)₂Cl (cis isomer), 65084-87-9; Ta(CO)₂-(DMDEPE)₂Cl (trans isomer), 65015-80-7; Nb(CO)₂(DMPE)₂Cl, 66507-17-3; Ta(η⁴-naphthalene)(DMPE)₂Cl, 64367-79-9; [(η-C₅H₅)₂Ta(DMPE)]PF₆, 73274-63-2; (η-C₅H₄Me)₂TaBr₂, 61202-67-3; [Ta(CO)₂(DMPE)₂Cl]⁺, 73274-64-3; [Ta(CO)₂(DMPE)₂Br]⁺, 73274-65-4; [Ta(CO)₂(DMPE)₂I]⁺, 73274-66-5; [Ta(CO)₂-(DMPE)₂CH₃]⁺, 73274-67-6; [Ta(CO)₂(DMPE)₂H]⁺, 73307-15-0.

(37) Bond, A. M.; Colton, R. *Inorg. Chem.* **1976**, *15*, 446.
(38) Bond, A. M.; Colton, R. *Inorg. Chem.* **1976**, *15*, 2036 and references therein.
(39) Bond, A. M.; Colton, R.; Jackowski, J. J. *Inorg. Chem.* **1979**, *18*, 1977.

(40) Saveant, J. M.; Binh, S. K. *J. Electroanal. Chem.* **1978**, *88*, 27.

Contribution of the Department of Chemistry,
University of Missouri, Columbia, Missouri 65201

Studies on the Rates of Isotopic Oxygen Exchange between Aquated Molybdenum(V) and Solvent Water

R. KENT MURMANN

A method is described which allows precise isotopic analysis of the less labile oxygen atoms in the first coordination sphere of Mo(V) in aqueous media. Rapid conversion of Mo^V(aq), as generated by Hg⁰ reduction of Mo(VI) in ca. 3 M HCl solution, to Mo₂O₄EDTA²⁻ in labeled water shows no appreciable transfer of solvent oxygens to the product ion. Aquated Mo(V), commonly referred to as Mo₂O₄²⁺, is shown to contain 1.98 ± 0.03 slowly and 2.04 ± 0.06 rapidly exchanging oxygens (on the minute time scale) in agreement with the formula Mo₂O₄²⁺(aq). The slowly exchanging oxygens are shown by Raman and IR ¹⁸O shifts to be the bridging type having a $t_{1/2}$ of about 100 h at 40 °C while the yl-oxygens have a $t_{1/2}$ of about 4 min at 0 °C. Solvent in the coordination sphere exchanges much more rapidly. Some of the kinetic parameters and medium effects are evaluated and discussed.

Introduction

A precise knowledge of the structural nature and exchange behavior of aquated metal ions is a prerequisite to future progress in reaction kinetics and mechanisms in aqueous media. However, our understanding of many of these ions has lagged

due to the difficulties involved in designing definitive experiments when the ligands are common to the solvent. Most structural information for ions in solution has been inferred from solid X-ray structures, and, fortunately, this has often been a reliable source, but, as more complete information is

required, reliance on extrapolations from solid structures will not be satisfactory.

Development in the field of Mo aquo ions is quite recent, with most of the structural information coming after 1970.[1] In acidic media, except for $[Mo(OH_2)_6]^{3+}$, all of the ions so far identified in the +2 to +5 oxidation states appear to be dimeric with either a metal–metal bond,[2] Mo_2^{4+}, and/or bridging oxo or hydroxo groups,[3] i.e., $Mo_2O_4^{2+}$. The evidence behind the structures is primarily their diamagnetism, quantitative ion-exchange measurements,[4] acid cryoscopic measurements,[5] and X-ray solid structures of complexes.[6]

Several recent studies have shown that oligomerization often produces species which are relatively nonlabile[7] and thus amenable to structural studies in solution. ^{18}O-exchange studies have been immensely helpful with other metal[8–10] oxyions, providing unambiguous answers to the question of the number of and lability of solvent and its ions in the first coordination sphere of a metal ions.

For acidic $Mo^V(aq)$ solutions, the present evidence supports[1] the dimeric cis structure with three distinguishable oxygen types. A coordination number of 6 is assumed without firm evidence.
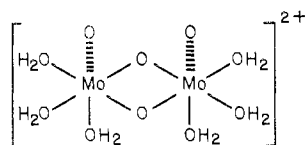

This ^{18}O-exchange study was begun with the expectation that some oxygens in the first coordination sphere of Mo(V) would be nonlabile and would allow a determination of the ionic formula in solution. Then a study of the kinetics of the isotopic exchange of these oxygens with solvent might provide an insight into the rate of opening of the dimeric structure and the fraction existing at equilibrium as the monomer.

Experimental Section

Sodium molybdate, $Na_2MoO_4\cdot2H_2O$, AR, the starting material for all molybdenum compounds used in this study was twice fractionally recrystallized from water. It was reduced in HCl solution with an excess of Hg^0 in a sealed vessel containing an argon atmosphere. Several days at room temperature were required for complete reduction. Typically the solutions were 0.1–0.4 M in MoO_4^{2-} and 1–5 M in HCl. The reduction is acid dependent, and, with low acid and high total Mo, some blue Mo(V)–Mo(VI) precipitates were formed because the reduction used H^+. However, gradually the molybdenum blue redissolved to give clear orange-brown solutions. The excess Hg^0 (and the Hg_2Cl_2 produced) was left in contact with the stock solutions, which ensured complete reduction, and when samples were removed by hypodermic syringe, the vessel was repurged with argon. Contact with stainless-steel needles was minimal (4–6 s). In some cases Pt needles were used with no apparent rate change.

The solutions were analyzed for total Mo by oxidation with H_2O_2 and precipitation as $BaMoO_4$, for Mo(V) by addition of an aliquot to excess $Fe(NH_4)(SO_4)_2$ solution and back-titration with standard Ce(IV) solution using ferroin indicator, and for HCl by dilution followed by absorption of the metal ion on a Dowex 50W-X2 resin in the H^+ form, titrating the acid evolved with base, and correcting for the $Mo_2O_4^{2+}$ absorbed. The concentrations found were in close

agreement with the makeup if we assumed the reaction

$$2Cl^- + 2Hg^0 + 8H^+ + 2MoO_4^{2-} \rightarrow$$
$$Hg_2Cl_2\downarrow + Mo_2O_4^{2+} + 4H_2O$$
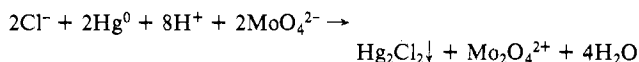
Within ±1%, the experimental precision, all of the molybdenum was in the +5 oxidation state after 3 days of reduction and remained so after 65 days at room temperature.

$[Pt(en)_2]Cl_2$ and $[Pt(en)_3]Cl_4$ were prepared by direct reaction of $PtCl_4^{2-}$ and $PtCl_6^{2-}$, respectively, with en and were doubly recrystallized.

Solvent water was distilled and deionized while ^{18}O-enriched water was triply distilled, once from alkaline MnO_4^-, once from acid CrO_4^{2-}, and once without additions. The deuterium content was normalized. Salts used in the kinetic studies were recrystallized from AR quality reagents.

Analyses for C, H, N, and Mo were the courtesy of the University of Illinois Chemistry Analytical Service. Isotopic measurements were made on CO_2 purified by VPC utilizing a Nuclide RMS-16 mass spectrometer. The $46/(44 + 45)$ ratio, R, was measured and compared to a standard CO_2 sample whose R_n was arbitrarily set at 4.00×10^{-3}. Conversion of the solid salts containing oxygen to CO_2 was accomplished by heating in a sealed tube at 425 °C for 2 h with $Hg(CN)_2$–$HgCl_2$, $Hg(CN)_2$, AgCN, or $(CN)_2$. The gaseous products were collected under vacuum, and the CO_2 was quantitatively separated by VPC and analyzed. For most solid samples, AgCN is the reagent of choice, being less poisonous than the Hg salts while providing sufficient gas. $(CN)_2$, while convenient, produced considerably less gas.

^{18}O-**Exchange Kinetics.** Early in the study it was established that EDTA in any of its protonated forms or in Mo(V) complexes does not exchange its carboxyl oxygens with solvent in dilute acid or base over a period of 5 days at 25 °C. Further, it was demonstrated that $Mo_2O_4^{2+}$ solutions could be quickly (<10 s at 0 °C) and quantitatively (>99%) converted[11] to $Mo_2O_4EDTA^{2-}$, a complex of known structure even in solutions initially 1.5 M in HCl by the addition of excess Na_2EDTA under appropriate conditions. Also, it was established that all the oxygens in $Mo_2O_4EDTA^{2-}$ were nonlabile, and less than 1% exchange with neutral solvent occurred in 3 days at 25 °C.

Since no suitable precipitating agent was found for $Mo_2O_4^{2+}$, it was converted to $Mo_2O_4EDTA^{2-}$ and crystallized with either $Pt(en)_3^{4+}$ or $Pt(en)_2^{2+}$. The latter was found later in the study to be superior since it had better physical characteristics and was more selective. Conversion to the EDTA complex and crystallization as either platinum salt induced about 2% exchange in the yl-oxygens and no observable exchange in the bridging or EDTA oxygens. The salts are hydrated when obtained from solution but are quickly and completely dehydrated under vacuum (10^{-5} mm) at room temperature.

Anal. Calcd for $PtMo_4C_{26}H_{48}N_{10}O_{24}$ ($[Pt(en)_3][Mo_2O_4EDTA]_2$ (anhydrous), mol wt 1463.58): Mo, 26.22; N, 9.57; C, 21.34; H, 3.31; Pt, 13.33. Found: Mo, 25.99; N, 9.34; C, 20.67; H, 3.28; Pt, 13.47. Calcd for $PtMo_2C_{14}H_{28}N_6O_{12}$ ($[Pt(en)_2][Mo_2O_4EDTA]$ (anhydrous), mol wt 859.38): Mo, 22.33; N, 9.78; C, 19.57; H, 3.28; Pt, 22.70. Found: Mo, 22.62; N, 9.57; C, 19.83; H, 3.30; Pt, 21.91. Calcd for $PtMo_4C_{26}H_{56}N_{10}O_{28}$ ($[Pt(en)_3][Mo_2O_4EDTA]_2\cdot4H_2O$, mol wt 1535.64): H_2O, 4.69. Found: H_2O, 4.81.

A rate determination for the faster exchanging oxygens consisted of injecting 0.500 mL of a stock solution of $Mo_2O_4^{2+}$ in normal water into 5.00 mL of about 3 times enriched water containing the appropriate amounts of acid and salt. The reactants were at 0 °C at the time of mixing and were maintained at this temperature by an ice–water bath. An argon atmosphere was constantly held in the sealed vessel. At timed intervals, 1-mL samples were removed and immediately injected into 1.0 mL of a saturated Na_2EDTA solution at room temperature. An initial cloudiness developed, clearing in a few seconds, followed by crystallization of the excess EDTA. After 1 h at 0 °C, centrifugation separated the EDTA, and the supernatent solution was treated with 5 drops of saturated $[Pt(en)_2]Cl_2$ solution. After nucleation and crystallization, the orange product $[Pt(en)_2][Mo_2O_4EDTA]\cdot4H_2O$ was collected, washed with cold water and methanol, and dried under vacuum (10^{-5} mm) in a break-seal tube. For isotopic analysis it was converted to CO_2 as previously described. Normal ^{18}O values for the EDTA oxygens and for the initial and final

(1) M. Ardon and A. Pernick, *J. Less-Common Met.*, **54**, 233 (1977).
(2) A. R. Bowen and H. Taube, *J. Am. Chem. Soc.*, **93**, 3287 (1971).
(3) M. Ardon and A. Pernick, *J. Am. Chem. Soc.*, **95**, 6871 (1973).
(4) M. Ardon and A. Pernick, *Inorg. Chem.*, **12**, 2484 (1973).
(5) M. Ardon, A. Bino, and G. Yahav, *J. Am. Chem. Soc.*, **98**, 2338 (1976).
(6) S. Khalil, B. Sheldrick, A. B. Soares, and A. G. Sykes, *Inorg. Chim. Acta*, **25**, L83 (1977).
(7) R. K. Murmann and K. Giese, *Inorg. Chem.*, **17**, 1160 (1978).
(8) H. Goff and R. K. Murmann, *J. Am. Chem. Soc.*, **93**, 6058 (1971).
(9) H. Gamsjäger and P. Baertschi, *Helv. Chim. Acta*, **55**, 2154 (1972).
(10) A. Okumura and N. Okazaki, *Bull. Chem. Soc. Jpn.*, **46**, 2937 (1973).

(11) Yoichi Sasaki and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, 1468 (1974).

solvents were determined in the usual manner.

A representative rate run of ^{18}O exchange for the slower oxygens of $Mo_2O_4^{2+}$ involved adding 1–2 mL of ^{18}O-enriched $Mo_2O_4^{2+}$ stock solution to 50.00 mL of solvent containing the appropriate acid and salts and holding the mixture at 0 °C for about 1 h to allow the faster oxygens to equilibrate with the solvent. The reactants were quickly brought to temperature, usually 40 °C, and 10–12-mL samples taken. These were cooled to 0 °C, diluted by a factor of 2–4 depending on the (acid + salt) concentration, and absorbed on a purified 50W-X2 resin in the Na^+ form. The $Mo_2O_4^{2+}$ on the resin was washed with H_2O for about 3 min at room temperature to allow the yl-oxygens to normalize. Care must be taken not to allow longer periods in neutral media because oxidation to Mo-blue compounds easily takes place which causes ^{18}O exchange. The ion was removed from the resin by reaction with 0.1 M Na_2EDTA solution and crystallized by the addition of $Pt(en)_2^{2+}$. The orange solid was collected and treated as previously described, giving CO_2 for isotopic analysis.

Infrared Analysis. A preparation of $[Pt(en)_2][MoO_2{}^{18}O_2EDTA]$ in which the ^{18}O is in the fast-exchanging positions was accomplished by allowing exchange with ^{18}O water to occur for a limited time. About 1.0 mL of water (69% ^{18}O) was distilled under vacuum into a container, and 0.25 mL of a $Mo_2O_4^{2+}$ solution ~0.4 M with 3 M HCl was added while both were held at 0 °C. The mixture was allowed to equilibrate for 30 min at 0 °C ($t_{1/2}$ = 4 min at 0 °C), an excess of solid Na_2EDTA was added, and after 30 min at room temperature the water was transferred under vacuum and recovered. Fifteen milliliters of normal H_2O was added, and the solids were removed by centrifugation. $[Pt(en)_2][Mo_2O_4EDTA]\cdot4H_2O$ was crystallized by the addition of $Pt(en)_2^{2+}$ solution, washed with 0 °C water and methanol, and air-dried. The purity required necessitated a crystallization from 10 °C water. The product was estimated to have about 45% ^{18}O in the fast exchanging oxygens and less than 0.4% ^{18}O in the slow positions. IR spectra were taken on Nujol mulls with a Perkin-Elmer Model 10 spectrometer of the normal and the ^{18}O-enriched salt.

Laser Raman Spectra. As a second, more definitive check on the molecular position of the more rapidly exchanging oxygen, a solution (about 3.5 M) of $Mo_2O_4^{2+}(aq)$ was diluted by 4 times its volume with ^{18}O water. The Raman spectra were taken over the periods of 3–8 and 10–15 min from the time of mixing. The temperature was ~24 °C, but local heating occurred at the liquid surface. A laser wavelength of 5147 Å was used, and the double monochromator had a selectivity of 0.1 wavenumber.

Kinetic Data Treatment. The kinetic data were treated according to the expression

$$-\ln (1 - F) = k_{obsd}t$$

where $R = k_{obsd}(AB)/(A + B) = k[Mo_2O_4^{2+}]$, A = [exchanging oxygens] = $2[Mo_2O_4^{2+}]$ for each type, and B = [solvent]. With dilute solutions, $(A + B) \approx B$ and $k = 2k_{obsd}$. In the noted situations, plots of $-\ln (1 - F)$ vs. time were not linear. The treatment and interpretation are given in the discussion. Values for $(1 - F)$ were calculated from $(R_0 - R_\infty)/(R_t - R_\infty)$, where R represents the $46/(44 + 45)$ ratio of the mass to charge on ions from CO_2. No corrections were made for the small kinetic or equilibrium isotope effects, for the slight nonlinearity of R with atom percent, and the measured samples were always less than 4 times normal enrichment, which was in the linear region of the instrument.

Results

When this study was begun, there was no way of predicting if any of the atoms in the first coordination sphere of Mo(V) would be held back from exchange with the solvent in the minimum time of separation (estimated to be about 5 s). Also the formation of the known ion $Mo_2O_4EDTA^{2-}$ might occur with appreciable, or complete, oxygen exchange with the solvent. These questions had to be settled before the oxygens could be "counted" or their kinetic properties evaluated.

EDTA–H_2O Exchange. Several experiments were carried out in which EDTA in its various complex and protonated forms in the pH range 2–7.5 was equilibrated with enriched water at 25 °C for 1 day. The EDTA was isolated anhydrous, and its ^{18}O content was not enriched. The precision was about 2% of the possible change, larger than usual due to the difficulty of completely drying the EDTA. This lack of exchange is in agreement with that observed for substituted acetic acids[12]

Table I. Solvent Oxygen Exchange and Transfer[a]

$$Mo^V(aq) + H_2{}^{18}O \xrightarrow{EDTA} [Mo_2O_4(EDTA)]^{2-}$$

oxygen source	$10^3 R_n$	oxygen source	$10^3 R_n$
$Mo_2O_4^{2+}$	4.01	calcd	3.99
EDTA	3.98	(zero exchange)	
H_2O solvent	8.73	calcd	5.57
$Mo_2O_4EDTA^{2-}$ [b]	4.04	(complete exchange)	

% exchange: 3.2

av % zero-time exchange (18 expts): 2.9

[a] 0 °C, short contact time. [b] Found at $T = 0$.

under similar conditions. In several experiments, a small quantity of Mo(V) was present which became complexed, but no O exchange on the EDTA was found.

$Mo_2O_4EDTA^{2-}$–H_2O Exchange. In a kinetic study[13] of the acid–base dependence of the oxygen exchange with this and related complexes, it was found that no exchange, ±1%, with any oxygen in the complex occurred over a period of 2 days at room temperature in mildly acidic or basic solutions. The acidity range in that study covered the entire range used in the formation of the complex and workup in the work described here.

Mo(V) → $Mo_2O_4EDTA^{2-}$: Oxygen Transfer. In these experiments, normal (normal ^{18}O content) Mo(V) in normal water was added to ^{18}O-enriched HCl–H_2O solution at 0 °C, and, within 1 s, excess Na_2EDTA solution (25 °C) was added. Visually it was estimated that the $t_{1/2}$ for complex formation was no larger than 1–2 s. Thus we were competing the exchange of oxygen on Mo(V) with the conversion to the complex ion. ^{18}O analysis of the complex ion showed that it contained only a slight enrichment corresponding to about 3% exchange on the non-EDTA oxygens (Table I). This exchange could come from the few seconds of exchange on $Mo^V(aq)$ during its average lifetime before it is complexed with EDTA, or it could come during the formation of the EDTA complex. The former is probably correct, and exchange is probably enhanced by the momentary low-acidity conditions (which are shown later to speed up the exchange) brought about by the addition of Na_2EDTA. *These studies prove that the four oxygens attached to Mo in $Mo_2O_4EDTA^{2-}$ come from the first coordination sphere of $Mo^V(aq)$ and not from the solvent.* Further, the rate of exchange of these oxygens is slow enough for conventional kinetic studies.

Number of Oxygens of Each Type. The initial kinetic experiments were conducted only for short times, and it became apparent that the half-life was about 5 min at 0 °C, but only half of the oxygens of the product $[Pt(en)_2][Mo_2O_4EDTA]$ were exchanged in 10 half-lives. No further exchange was observed at 0 °C in 1 day.

At elevated temperatures, 40 °C, the other two oxygens were found to exchange with the solvent at a reasonable rate. Since the rates of exchange were so widely separated, the composition of the solid $[Pt(en)_2][Mo_2O_4EDTA]$ was known, and all oxygen in it became completely mixed and equilibrated during the conversion to CO_2, it was possible to accurately count the number of oxygens of each type. Experimental constraints provided the greatest accuracy when we followed the uptake of ^{18}O from the solvent for the faster oxygens and the loss of ^{18}O from the enriched complex for the slower oxygens. However, following the reaction in either direction was completely consistent with two pairs of two oxygens each. Tables II and III give examples of each type of experiment and

(12) D. R. Llewellyn and C. J. O'Connor, *J. Chem. Soc.*, 545 (1964).
(13) P. Robinson, C. R. Landis, and R. K. Murmann, paper presented at the 3rd International Conference on the Chemistry and Uses of Molybdenum, University of Michigan, 1979.

Table II. Solvent Exchange with Mo^V(aq): Determination of the Number of Rapidly Exchanging (yl) Oxygens

oxygen source	$10^3 R_n$	oxygen source	$10^3 R_n$
$Mo_2O_4^{2+}$	4.01	calcd	3.99
EDTA	3.98	(zero exchange)	
H_2O solvent	27.31^a	calcd	7.87
$Mo_2O_4EDTA^{2-}$ ^{b}	7.91	$(Mo_2O_4EDTA^{2-})^c$	

no. of oxygens exchanged (exptl): 2.021
av no. of oxygens (12 expts): 2.04 ± 0.06^d

^{a} This value did not change significantly during exchange. ^{b} After 40 min at 0 °C. ^{c} Two exchanging oxygens. ^{d} This value may be slightly high due to a small amount of exchange with the second type of oxygen.

Table III. Solvent Exchange with Mo^V(aq): Determination of the Number of Slowly Exchanging (Bridging) Oxygens

oxygen source	$10^3 R_n$	oxygen source	$10^3 R_n$
$Mo_2O_2{}^{18}O_2{}^{2+}$	4.23, 12.89^a	$Mo_2O_4(EDTA)^{2-}$ ^{d}	4.07
EDTA	3.98	(exptl)	
solvent^d	4.23^b	$[Mo_2O_4(EDTA)]^{2-}$ ^{d}	4.06
calcd (zero; all oxygens)	5.507	(calcd)	

no. of oxygens exchanged (exptl): 1.986^c
av no. of oxygens exchanged (17 expts): 1.98 ± 0.03

^{a} Obtained from initial value of the uniformly labeled complex and from the solvent with which it was half-exchanged. ^{b} This value did not change significantly during exchange. ^{c} Calculated from the zero value and the experimental and calculated values (final). ^{d} Final.
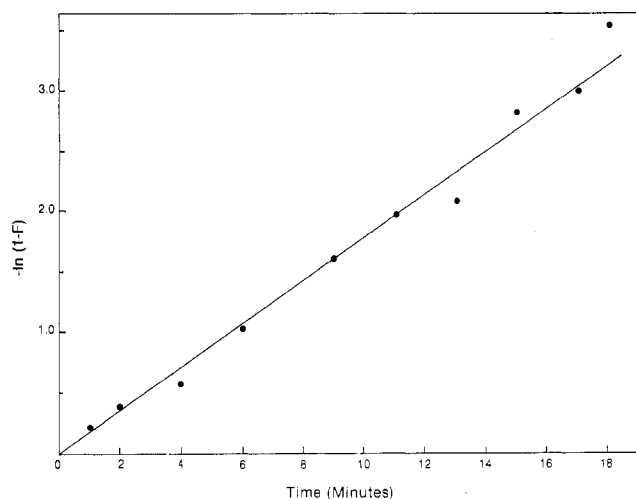
Figure 1. Rate of ^{18}O exchange of $Mo_2O_4^{2+}$ at 0 °C (fast oxygens; run 8); $[Mo_2O_4^{2+}] = 0.0208$ M, $[H^+] = 0.464$ M, $[Na^+] = 0.083$ M.

summaries of all data collected which allowed the calculation of the oxygen-exchange number.

Kinetics of Oxygen Exchange—Fast Oxygen. Figure 1 shows a representative example of the first-order kinetic graph measured after the final techniques had been optimized. The zero-time exchange was typically 1–3% (corrected for in Figure 1), and no curvature was apparent. Because of the rapidity of the reaction and perhaps a variability in the induced exchange, the precision of the rates observed is not as good as normally obtained. However, the major features of the rate expression are apparent. From the summary in Table IV the rate of ^{18}O exchange is independent of acidity (0.01–3.1 M), first order in complex ion concentration, not highly (if at all) light sensitive, and reproducible from one preparation to another and gives the same result with either precipitating cation.

Table IV. Summary of yl-Oxygen-Exchange Measurements on $Mo_2O_4^{2+}$ (0 °C)

run	complex	$[Mo_2O_4^{2+}]$, M	$[H^+]$,^{d} M	atm	$t_{1/2}$,^{c} min
$1^{a,b}$	normal	0.0167	0.833	air	4.1 ± 0.5
2	enriched	0.0181	0.846	air	3.9 ± 0.7
3	normal	0.0167	0.833	air	4.0 ± 0.2
4^f					
5	normal	0.0208	0.464	air	4.5 ± 0.2
6	normal	0.0208	0.464	Ar	3.9 ± 0.2
7	normal	0.0208	0.464	Ar	3.9 ± 0.1
8^e	normal	0.0208	0.464	Ar	3.9 ± 0.1
9	enriched	0.0167	0.667	Ar	4 ± 1
10	enriched	0.0315	3.1	Ar	3.5 ± 0.5
11	normal	0.0173	0.387	Ar	3.4 ± 0.2
12	normal	0.0195	0.083	Ar	3.6 ± 0.2
13	normal	0.0194	0.187	Ar	4.2 ± 0.2
14	normal	0.0102	0.043	Ar	4.20 ± 0.1
15	normal	0.0194	0.295	Ar	3.90 ± 0.2
16	normal	0.0390	0.165	Ar	3.52 ± 0.1
17	normal	0.0021	0.0090	Ar	3.53 ± 0.2

^{a} Precipitating agent: runs 1–6, $Pt(en)_3^{4+}$; runs 7–17, $Pt(en)_2^{2+}$. ^{b} Runs 1–5 in air, runs 7–17 under argon, and run 3 in the dark. ^{c} $k_{av} = (5.96 \pm 0.60) \times 10^{-3}$ s^{-1}; ± values = 1 standard deviation of the mean. ^{d} As HCl. ^{e} 0.1 M NaCl also present. ^{f} Zero and infinite determinations.
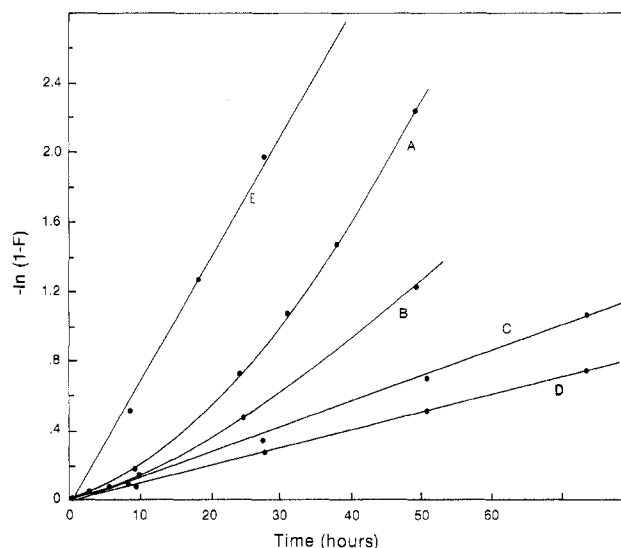
Figure 2. $Mo_2O_4^{2+}$–^{18}O exchange (slow oxygens; 40 °C): A, 0.062 M H$^+$; B, 0.112 M H$^+$; C, 0.112 M H$^+$; D, 0.162 M H$^+$; E, 1.061 M H$^+$ (Hg^0 present in C, D, and E).

Small quantities of air in the argon atmosphere did not affect the rate, but over a longer period of time, i.e., for the ∞ value, some differences were found, indicating that small amounts of another substance, presumably MoO_4^{2-}, were being formed through disproportionation or air oxidation. A temperature dependence was not attempted due to the rapidity of the reaction and the inherent errors in measurement.

Kinetics of Oxygen Exchange—Slow Oxygen. In most cases this exchange was followed by measuring the loss of ^{18}O from the enriched complex ion. The initial experiments showed curved McKay graphs, Figure 2, indicating some chemical reaction taking place in addition to the exchange increasing the isotopic exchange rate. The chemical composition and the IR spectra of the isolated solid $[Pt(en)_2][Mo_2O_4EDTA]$ were unchanged during the exchange reaction. It seemed likely that oxidation or disproportionation was responsible and that the products of that reaction were not isolated. The presence of Hg^0, with occasional shaking, gave linear behavior, while an increase in the [HCl] improved the linearity of the McKay plot, but the presence of Ag^0 or Sn^{2+} had little effect. (Hg^0

Table V. Rates of Bridging-Oxygen Exchange on $Mo_2O_4^{2+}$

run	$10^3[Mo_2O_4^{2+}]$, M	$[H^+]$, M	$t_{1/2}$, h	linear	temp, °C	$10^6 k_{obsd}$, s^{-1}
1	1.55	0.0624	26.65	no	40	7.22[c]
2	1.55	0.1124	48	no	40	4.01[c]
3	1.55	0.1624	68.0	yes?	40	2.83[c]
4[a]	1.55	0.1124	48.2	yes	40	3.99
5[b]	1.55	0.1624	7.28	yes	40	26.4
6	1.55	0.2624	70.1	yes	40	2.75
7[a]	2.39	0.304	96.0	yes	40	2.01[c]
8[d]	2.39	0.304	62.0	no	40	3.11[c]
9	2.39	0.548	43.0	no	40	4.48[c]
10[a]	2.39	0.304	413.0	yes	25	0.466
11[a]	2.39	0.304	3.94	no	60	48.8[c]
12[a]	2.39	0.304	2427.0	yes	15	0.0793
13[a]	2.39	1.061	9.44	yes	40	20.4
14[b]	2.39	1.061	9.20	no	40	20.9[c]
15[e]	2.39	0.304	4.37	?	40	44.0[c]
16[f]	2.39	0.304	44.6	yes	40	4.32
17[a]	2.39	0.861	14.3	yes	40	13.5
18[g]	2.39	0.304	99.7	yes	40	1.93
19	2.39	0.304	48.5	yes	40	3.97
20	2.39	0.304	28.4	yes	40	6.67
21	2.39	0.304	8.74	yes	40	22.0
22	2.39	0.304	3.77	yes	40	51.1

[a] Hg^0(l) present; intermittent stirring; $[Na^+] \approx 0.004$ M; $\mu = [HCl] + [NaCl]$. [b] Na_2MoO_4 present, 5.0×10^{-4} M. [c] Initial stage. [d] Ag metal sheet present, ~10 cm². [e] $[SnCl_2] = 2.00 \times 10^{-3}$ M. [f] 0.25 M in NaCl. [g] Runs 18–22, $10^4[Mo(VI)]$ added: (18) 0.2 M, (19) 1.0 M, (20) 2.0 M, (21) 5.0 M, (22) 10.0 M.
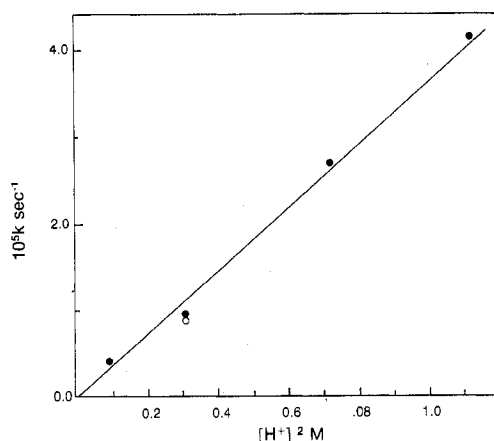

Figure 3. Exchange of ^{18}O between $Mo_2O_4^{2+}$ and water (slow oxygens; 40 °C): ●, HCl; ○, HCl + 0.025 M NaCl.

Figure 4. Effect of MoO_4^{2-} on $Mo_2O_4^{2+}$ oxygen exchange (runs 18–22; 40 °C; slow oxygens).

is known to reduce Mo(VI) to $Mo_2O_4^{2+}$, Sn^{2+} reacts with Mo(VI) in acid giving an unkown product, and Ag^0 appears to react very slowly if at all.) The curvature of the McKay plots was highly reproducible and did not appear to reflect the care with which the solutions were flushed with argon after samples were taken. This suggests a slow disproportionation or reduction of water. In the higher acid regions the graphs became linear for at least 1 half-life, and rate parameters could be evaluated. Apparently Hg^0 maintains a small and constant concentration of Mo(VI) by reduction of it at a relatively rapid rate at 40 °C, giving linear McKay graphs.

Table V summarizes the results obtained. On the basis of only one observation (runs 16 and 18), the reaction appears to be dependent on ionic strength at a constant acid concentration. The acid dependency is given in Figure 3, being second order (not at constant ionic strength). Considerable difficulty was encountered at high ionic strength, especially with use of NaCl, due to the large volumes generated upon dilution which was necessary to ensure complex-ion absorption on the ion-exchange resin. This resulted in excessive column times and a subsequent uncertainty in the quenching time. So, the effect of salts on the rate is not known precisely and the increase in the rate constant may be due to acidity, ionic strength, or Cl⁻, or a combination of these. The effect of [Mo(VI)] on the
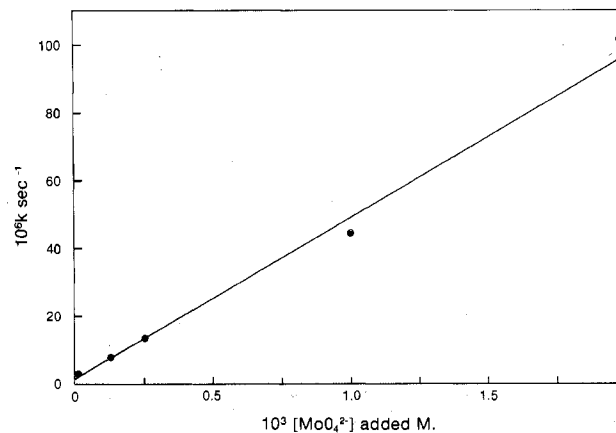
reaction rate is presented in Figure 4. A marked catalysis occurs which is first order in MoO_4^{2-} added. Under the acidity conditions used, the Mo(VI) most certainly exists as oligomers of unknown structure and complexity. Its effect provides a rationale for the curved McKay plots (Figure 2), since either disproportionation or water reduction would give Mo(VI) and catalysis. In 0.30 M HCl the molybdenum(VI) dependence may be expressed by $k = k_0 + k_1[Mo(VI)]$ with $k_0 = 4.0 \times 10^{-6}$ s^{-1} and $k_1 = 4.6 \times 10^{-2}$ s^{-1} M^{-1} at 40 °C. A calculation, based on Figure 3, graph A at its maximum slope, and k_1, gives about 5% conversion of Mo(V) to Mo(VI) in about 50 h at 40 °C. The temperature dependence of the rate of exchange was evaluated with four determinations in the range 15–60 °C in 0.30 M HCl. A good linear dependence of ln k vs. $1/T$ was obtained, and the activation parameters were obtained with linear least-squares analysis by assuming the transmission coefficient to be 1 and the error to be entirely in the rate constants: $\Delta H^\ddagger = 25.9 \pm 1.6$ kcal M^{-1}; $\Delta S^\ddagger = 0.4 \pm 0.2$ cal M^{-1} deg^{-1}. The calculated half-time at 0 °C is about 1200 days in 0.3 M HCl solution.

Identification of Fast and Slow Sites of Exchange. An examination of the IR spectra of the ^{18}O-enriched and normal EDTA complex shows a change in the 950-cm^{-1} region but not in the 760-cm^{-1} region. Some difficulty in interpretation

Table VI. Laser Raman Spectra of Aquated Mo(V) in H$_2$O^a

|	freq, cm^{-1}	
	bridging oxygen	yl-oxygen
no ^{18}O	756	982.2
3–8 min contact time	752.1	980.8, 931.0
10–15 min contact time	749.9	976.4, 925.4

^{a} Exciting wavelength 5147 Å (19 428 cm^{-1}).

occurs due to overlapping with the EDTA and en bands. The ^{18}O water was normalized with respect to the deuterium, and so substitution for the N–H in en is not a problem. It is clear that the band at 760 cm^{-1}, usually attributed to the Mo–O–Mo entity,[14] does not change (760 ± 1 cm^{-1}) upon ^{18}O enrichment of the complex ion when only enough time is allowed for one type of oxygen to exchange. In the Mo–O region,[14] however, the usual band at 954 cm^{-1} is shifted to about 902 cm^{-1}. The calculated shift on the basis of reduced mass would be to 907 cm^{-1}. The results strongly suggest that fast exchange occurs on the yl-oxygen with no appreciable exchange with the bridging oxygen in the time allowed (5–13 min). The conclusion is not completely convincing however. A way around the absorption by the EDTA and en ligands is to use the free Mo(V) ion and the laser Raman spectra. The results of this study are presented in Table VI.

In the presence of ^{18}OH$_2$, a new band appears at 930 cm^{-1} (calculated 934 cm^{-1}) and the 980-cm^{-1} band (yl-oxygen) diminishes. No significant change was found in the 750-cm^{-1} band or at the calculated lower energy region (713 cm^{-1}). The results confirm that the yl-oxygen is the rapidly exchanging one. Due to the final ^{18}O content of the solvent being about 50%, the two yl-type isotopic absorption peaks were expected and were found to be of roughly equal intensity.

With both the yl- and bridging-oxygen rate experiments a few trials were made in which the aliquots were treated with buffered base to a pH of about 5 before the Na$_2$EDTA was added. Invariably, extensive exchange occurred during the brief time the solutions were at near neutrality. This could have been due to Mo(VI) generation through air oxidation and its catalysis or due to an OH$^-$ term in the rate equations. The latter seems the more likely due to the lack of observation of Mo(VI) as a Mo blue and the short exposure time.

Of considerable interest is the information this study gives on the rate of opening of the
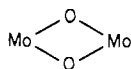
bridges and the fraction of monomer present at equilibrium. During the opening of the bridge and subsequent re-formation, it is reasonable to expect considerable if not complete exchange

with the solvent in a very short period of time.
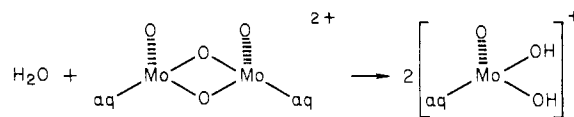
If that is the case, then the rate of opening the bridging ring must be of the same order of magnitude as or smaller than the rate of ^{18}O exchange of the bridging oxygens. This conclusion is reached whether one considers the ring opening to give the monomer or a singly bridged species.

The zero-time exchange averaged about 2%, never exceeded 3%, and was not related to the complex concentration. Formation of the EDTA complex and its subsequent precipitation were essentially quantitative ($\sim$95%) and would produce exchange if formed from the monomer. Thus an upper limit to the dissociation quotient can be made. With $C_0 = 1.55 \times 10^{-3}$ and no more than 5% zero-time exchange, the quotient [monomer]^2/[dimer] can be no greater than 4×10^{-6} at 40 °C. More precise measurements of the zero-time exchange and the order with respect to complex ion have to be made at much lower concentrations in order to obtain a useful value for this constant. This is in agreement with the observation of the rather complete loss of paramagnetism of aqueous solutions of (NH$_4$)$_2$MoOCl$_5$ and its dimerization to the ion of this study.[15]

Summary

Mo^V(aq) as prepared by the reduction of MoO$_4^{2-}$ by Hg^0 in acidic media shows two types of slowly exchanging oxygens per molybdenum. On conversion to [Mo$_2$O$_4$EDTA]$^{2-}$ all four Mo oxygens are transferred with less than 2% exchange with the solvent. Thus the exchange data are in agreement with the formulation
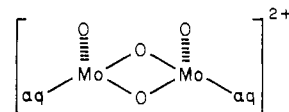
for the aquo ion. From Raman and IR measurements the two types have been identified as fast = yl and slow = bridging. The yl-oxygens exchange with $t_{1/2} \approx 4$ min at 0 °C while the bridging oxygens have a $t_{1/2}$ of $\sim$100 h at 40 °C (0.3 M HCl). The bridging-oxygen rate equation is second order with respect to [HCl] added and has an appreciable salt effect. Mo(VI) catalyzes the exchange of the bridging oxygens.

(14) W. E. Newton and J. W. McDonald, *J. Less-Common Met.*, **54**, 51 (1977).

(15) L. Scconi and R. Cini, *J. Am. Chem. Soc.*, **76**, 4239 (1954).