either from the solvent or from minor traces of water) follows the first electron-transfer step and yields HO(O)Mo(TPP), which has a reduction potential at $E_{1/2} = -0.1$ V. Afterwards, a second one-electron-transfer reaction can take place at the potential of reaction 8, producing an overall apparent two-electron-transfer reduction.

A similar mechanism as shown in eq 8–10 was also observed at 223 K, and attempts to spectrally identify the site of the first reduction (i.e., metal, oxygen atom, or ring based) were unsuccessful due to the rapid protonation (eq 9) yielding (OH)OMo(TPP). Previous studies of the bis(peroxo)molybdenum(VI) complex $(O_2)_2Mo(TmTP)$[26] have shown that an initial one-electron reduction occurs at the metal center, yielding a Mo(V) species. This possibility cannot be ascertained or ruled out in the present case.

In summary, although the reactivity of **1** is much lower than that of higher valent iron porphyrin complexes, the dual behavior observed—oxygen ligand transfer, in the case of phosphine oxidation, or an initial one-electron reduction either by hydrogen abstraction or at an electrode—seems to be related to the commonly accepted mechanism for oxidation by cytochrome P_{450}.

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[24] Analysis of the peak potentials and current–voltage curves fit the case of an ECE mechanism (electrochemical step followed by the chemical conversion to another electroactive species) where both electron transfers are reversible and the second reduction occurs at an $E_{1/2}$ positive of the first reduction. This thus leads to currents suggesting an apparent overall two-electron-transfer reaction.[25]

[25] Nicholson, R. S.; Shain, I. *Anal. Chem.* **1965**, *37*, 178.

[26] Kadish, K. M.; Chang, D.; Malinski, T.; Ledon, H. *Inorg. Chem.* **1983**, *22*, 3490.

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Articles

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Studies on the Kinetics and Mechanism of Oxygen Exchange between Solvent Water and $[MoOCl_5]^{2-}$

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A study of the ^{18}O exchange between HCl solutions of K_2MoOCl_5 and water indicates that the major ionic species in >10 M HCl is $[MoOCl_5]^{2-}$ and that the half-time for exchange is highly dependent on acidity, $[Cl^-]$, and $[Mo]_t$. At constant $[Mo]_t$ and acidity the isotopic-oxygen-exchange rate follows first-order kinetics with a small, consistent, time-zero exchange. In aqueous solutions containing only HCl and K_2MoOCl_5, the rate constant shows a minimum at about 11 M HCl; $k_{obsd} = 0.91 \times 10^{-4}$ s^{-1} at $[Mo]_t = 3.23 \times 10^{-2}$ M and 0 °C. Over an acidity range of 2.6–12.1 M HCl the rate follows the law $k_{obsd} = k_1[Mo]_t/[Cl^-] + k_2[Mo]_t^2[HCl]$ where $k_1 = (1.49 \pm 0.15) \times 10^{-4}$ M s^{-1} and $k_2 = (1.73 \pm 0.33) \times 10^{-4}$ M^{-2} s^{-1} at 0 °C and I = 12.1–12.3; $\Delta H^* = 64.2 \pm 0.2$ kJ/mol, and $\Delta S^* = -78.1 \pm 0.2$ J/(mol K). The kinetic results are interpreted in terms of the reversible formation of $[Cl_5Mo{-}O{-}MoCl_5]^{2-}$ in the most acidic media and the internal electronic rearrangement of the hydrolysis product, $[MoO(OH_2)Cl_4]^-$, at lower $[Cl^-]$. It is concluded that even in 2 M HCl the major ion present is $[MoOCl_5]^{2-}$ provided the total $[Cl^-]$ is >12 M. $[MoOBr_5]^{2-}$ is somewhat faster exchanging and shows the same general features.

Introduction

For some years now there has been an interest in the mechanism of oxygen exchange between solvent water and oxo, hydroxo, and aquo metal ions, but little definitive progress has been made. The advent of methods for measuring very fast reaction rates, i.e. NMR, stopped-flow, temperature-jump, etc., has allowed water-exchange rates for many aquo metal ions to be quantitatively studied, but even here our mechanistic understanding and our predictive capability are incomplete. ^{18}O-exchange methods, though limited to relatively slowly reacting systems, often give highly precise and significant results. The method is especially applicable to the kinetically slower oxo and hydroxo metal ions. A recent review of the subject[1] shows that only one mono-yl ion is known to exist in aqueous media, $VO^{2+}(aq)$, and its rate of oxygen exchange has been studied in detail.[2] Chloro–oxo complexes of the group 6 transtion-metal ions are known in the solid state and may also exist in solution, i.e. $[CrOCl_5]^{2-}$, $[MoOCl_5]^{2-}$, and $[WOCl_5]^{2-}$.[3-5] These ions, red, green, and green, respectively, form the basis of a mechanistically informative series. Our original intent was to carry out a comparative study with these

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[1] Gamsjäger, H.; Murmann, R. K. *Adv. Inorg. Bioinorg. Mech.* **1983**, *2*, 317–380.

[2] Johnson, M. D.; Murmann, R. K. *Inorg. Chem.* **1983**, *22*, 1068.

[3] Brown, D. *J. Chem. Soc.* **1964**, 4944.

[4] Allen, E. A.; Brisdon, B. J.; Edwards, D. A.; Fowles, G. W. A.; Williams, R. G. *J. Chem. Soc.* **1963**, 4649.

[5] Jørgensen, C. K. *Acta Chem. Scand.* **1957**, *11*, 73.

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Table I. Elemental Analyses

salt	% calcd		% found	
	Mo	Cl	Mo	Cl
K_2MoOCl_5	26.11	48.25	26.16	48.23
Cs_2MoOCl_5	17.29	31.94	17.31	32.08

ions with the expectation of obtaining mechanistic information, but the chemical properties of two of the ions prevented this. In particular, $[CrOCl_5]^{2-}$ hydrolyzes and is reduced rapidly and extensively even in concentrated HCl solution and $[WOCl_5]^{2-}$ oxidizes and disporportionates, preventing quality ^{18}O studies (in our hands at least) on both of these ions.

Molybdenum(V) is generally prepared in acidic media by stoichiometric reduction with Sn(II), NH_2NH_2, I^-, or Hg^0. The latter two methods were used in this study because the oxidation products, I_2 and Hg_2Cl_2, are easily removed. In concentrated HCl solution either paramagnetic $[MoOCl_5]^{2-}$ or $[MoOCl_4]^-$ can be nearly quantitatively separated from solution by the appropriate counterion, suggesting that both ions exist in solution. The formula of the product apparently depends on packing considerations in the solid lattice. Two dimers are postulated as the acidity decreases, para- and diamagnetic in that order,[6-8] but little is known definitively about their structure or formula. At lower acidities (<4 M) the diamagnetic $Mo_2O_4^{2+}(aq)$ is the predominate species in solution as shown by ^{18}O studies[9] and X-ray crystal structures[10] of solid complexes.

This study uses kinetic ^{18}O-exchange experiments to (a) establish the nature of the Mo(V) in concentrated HCl solution, (b) measure rates of exchange and suggest mechanisms for the exchange-rate terms, and (c) suggest equilibria occurring that result in oxygen exchange.

Experimental Section

$[MoOCl_5]^{2-}$ solutions were made from K_2MoOCl_5 prepared by the reaction (1 h at 80 °C) of MoO_3 with the calculated amount of KI in concentrated HCl solution. The liberated I_2 was removed by vacuum distillation, and the red solution was treated with anhydrous HCl gas. The resulting green solution was concentrated and again saturated with HCl gas whereupon dark green crystals of K_2MoOCl_5 were deposited. The KCl impurity was removed by selective solution in concentrated HCl and resaturating with HCl gas.[11] Several preparations were made that gave identical visible spectra agreeing with that of Haight[12] and having identical ^{18}O-exchange rates. For an estimation of the concentration of $[MoOCl_5]^{2-}$ in concentrated HCl solutions, measured extinction coefficients of 16.4 at 7050 Å and 15.6 at 4500 Å were used.

Solutions of HCl and LiCl were prepared from reagent grade materials and analyzed by acid titration (after proton ion-exchange replacement of Li). In Mo-containing solutions, titration was made directly to neutrality and correction made for the conversion of MoO^{3+} to $Mo_2O_4^{2+}$.

Several cations were investigated for precipitating $[MoOCl_5]^{2-}$, and Cs^+ was found to be highly satisfactory. Analyses were carried out on K_2MoOCl_5, which was used to prepare some of the solutions for oxygen exchange, and on Cs_2MoOCl_5, the precipitated salt in the ^{18}O-exchange studies. These are given in Table I. Cs_2MoOCl_5 is not hydrated, very insoluble in excess CsCl, easily washed, and not hydrolyzed by traces of water in the washing solvents. Some surface water or impurity was present in trace amounts on the solid and so it was always heated to about 250 °C under vacuum (10^{-4} mm) for a few minutes, which resulted in complete removal of the impurity without apparent O exchange.

The exchange rates were measured by following the increase in ^{18}O content of solid Cs_2MoOCl_5 as a function of time. Solutions of about 10-mL volume containing $[MoOCl_5]^{2-}$, HCl, and/or LiCl were equilibrated at the required temperature, and 1.00 mL of ^{18}O water ($\sim$12X normal enrichment) in $\sim$12 M HCl was added at the proper temperature to start the exchange. At timed intervals, 1–3-mL aliquots were removed (Pt needle and plastic syringe) and added to a CsCl–concentrated HCl solution at 0 °C. Precipitation occurred instantaneously. The solid was allowed to remain in contact with the mother liquor for 5 min and then removed by centrifugation, washed two times with a 50/50 MeOH–ether mixture at 0 °C and two times with absolute ether, and dried in a stream of dry argon. The light green solid was placed in a break-seal tube, and the tube was evacuated (10^{-4} mm). Then it was heated to 250 °C under vacuum for a minute or so and, after cooling, treated with a 50/50 (w/w) mixture of carefully dried $HgCl_2$ and $Hg(CN)_2$. After evacuation, the sealed tube was heated to 425 °C for 1.0 h in an oven and then cooled, and the gaseous contents of the tube were separated by VPC on a silicon oil on firebrick column. The CO_2 peak was collected, purified by vacuum distillation, and set aside for ^{18}O analysis. This was accomplished on a Nuclide RMS-16 dual-collector mass spectrometer by measuring the 46/(44 + 45) ratio. All values were normalized to a standard sample of CO_2 that was arbitrarily given the value of 4.000×10^{-3}. Low enrichments were used (less than 4X normal), and it has been shown that this is within the linear range of the instrument. The first-order kinetic plots were entirely linear (note exception in initial runs), sometimes to 95% completion, but there was always a nonzero intercept that did not vary significantly with any reactant concentration, temperature, or precipitating conditions. Neither was it affected by the length of contact with the mother liquor or the washing or drying conditions. It was highly reproducible and thus did not affect the observed rate constants, but we do not have a reasonable explanation for this behavior. The preparation and exchange studies on $[MoOBr_5]^{2-}$ were analogous to those of $[MoOCl_5]^{2-}$, but lower concentrations of the metal ion and HBr were necessitated by their physical properties.

Results

The first experiments were designed to determine whether slowly exchanging oxygens were present in the first coordination sphere of Mo(V) when in about 11.5 M HCl solution and to count their number. Freshly prepared and equilibrated solutions of K_2MoOCl_5 in concentrated HCl (10 mL) were treated with $^{18}OH_2$, 11.5 M in HCl (1 mL), both at 0 °C, and within 3 s (the time required for complete mixing) a few drops of CsCl saturated 11.5 M HCl solution were added. The salt produced, Cs_2MoOCl_5, contained only a very small ^{18}O enrichment, which corresponded to about 5% of the difference between the final solvent value and that of normal water. Numerous attempts to reduce this apparent induced exchange met with failure and showed only that the time-zero exchange was reproducible to ±2%. Some of the factors tested included lowering the temperature to −10 °C modifying the time of contact of the precipitate with the enriched solution, using differently prepared samples of $[MoOCl_5]^{2-}$, modifying the washing solvents and the washing procedure, drying in a different manner, drying the precipitate under vacuum without heat, looking for traces of exchangeable impurities in the solid by IR spectroscopy, and precipitating with CsCl solutions more highly ^{18}O enriched.

Since the product, Cs_2MoOCl_5, is anhydrous as shown by analysis and by IR measurements and 5% or less ^{18}O exchange occurs during the process of solution and precipitation, there is 1.0 ± 0.1 slowly exchanging oxygen attached to the ion in solution. Thus, the major species is MoO^{3+} coordinated with Cl^- and perhaps, under certain conditions, H_2O. By analogy with the other mono-yl ion whose structure has been established in solution, VO^{2+}, the group opposite the oxo group, is weakly held and easily replaced.[2] Crystal-packing energy differences could easily result in either $[MoOCl_5]^{2-}$ or $[MoOCl_4]^-$ being crystallized from solution by the appropriate counterion. The large charge on $MoO^{3+}(aq)$ of this d^1 system

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(6) Sacconi, L.; Cini, R. *J. Am. Chem. Soc.* **1954**, *76*, 4239.
(7) Hare, C. R.; Bernal, I.; Gray, H. B. *Inorg. Chem.* **1962**, *1*, 831.
(8) Haight, G. P., Jr. *J. Inorg. Nucl. Chem.* **1962**, *24*, 663.
(9) Murmann, R. K. *Inorg. Chem.* **1980**, *19*, 1765.
(10) Cotton, F. A.; Morehouse, S. M. *Inorg. Chem.* **1965**, *4*, 1377.
(11) James, R. G.; Wardlaw, W. *J. Chem. Soc.* **1927**, 2145.
(12) Reference 8, p 664.

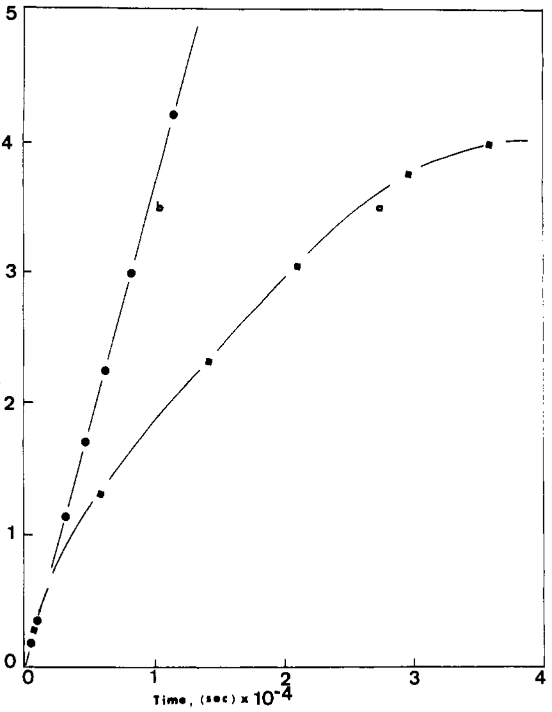

Figure 1. McKay plot for $[MoOCl_5]^{2-}$–H_2O exchange (0 °C; [HCl] = 12.3 M): (a) in flowing argon atmosphere; (b) in non-flowing air.

would be expected to produce extensive hydrolysis at low acidities in the absence of large concentrations of Cl^-, and spectral changes due to hydrolysis do occur outside the acid and Cl^- regions studied here.

The first rate experiments were conducted in about 12 M HCl solution, and a flow of argon was maintained over the exchanging solution to prevent oxidation by air, which we thought might occur. Figure 1a gives a McKay plot for a representative run of this type, which shows significant curvature toward slower rates at longer times. Tests proved the curvature to be due to the loss of HCl by vaporization into the argon purge gas. An identical run is given in Figure 1b in which an atmosphere of air was maintained (without flow). It is linear with a small zero-time intercept. In no case during this study have we observed evidence for air oxidation over the periods of the rate studies, which were as long as 12 h. The linear McKay plots established that only one aqueous species was present and that no chemical change was occurring during the exchange times. The values for k_{obsd} (s^{-1}) obtained from the slopes of the McKay plots reproduced to ±2% when the same stock solutions were used and ±5% when new stock solutions were used. The ± values are one standard deviation of the mean from a linear unweighted least-squares treatment of the data. The system was very well-behaved, and the largest deviations came from the inaccuracies in the solution concentrations at these high salt and or acid levels.

Table II summarizes all of the rate runs obtained. Each k_{obsd} represents five to seven points that agreed with a straight line with an agreement factor R greater than 0.97 and averaging 0.99.

Figure 2 summarizes the variance of k_{obsd} with [HCl] at a constant $[Mo(V)]_t$ of 0.0323 M. While it substantiates that the reason for the lowering of the rates was HCl loss when argon was passed over the exchanging media, the effects shown could be due to the changes in [HCl], $[H_{aq}^+]$, $[Cl^-]$, or I. In the 9.6 M HCl region, the effect of added Cl^- was investigated by increasing the total Cl^- concentration with LiCl to 11.8 M at constant HCl. The rate constant dropped considerably (runs 6 and 12) and became essentially identical with that obtained at 11.7 M in HCl alone (run 8).

Table II. Rate Constants of $^{18}OH_2$-$[MoOCl_5]^{2-}$ Exchange in HCl–LiCl Media at 0 °C

no.	$[[MoOCl_5]^{2-}]$, M	[HCl], M	[LiCl], M	10^4k, s
1	0.0646	12.30		3.36 ± 0.13
2	0.0323	12.23		1.74 ± 0.01
3	0.0485	12.27		2.56 ± 0.03
4	0.0162	12.19		0.858 ± 0.005
5	0.0081	12.18		0.468 ± 0.002
6	0.0323	9.69		1.84 ± 0.07
7	0.0323	10.71		0.970 ± 0.032
8	0.0323	11.72		1.18 ± 0.01
9	0.0323	11.21		1.01 ± 0.02
10	0.0323	10.20		1.20 ± 0.03
11	0.0323	13.98		4.05 ± 0.29
12	0.0323	9.68	2.06	1.20 ± 0.02
13	0.0323	9.23		3.66 ± 0.23
14	0.0395	11.73	0.52	2.24 ± 0.09
15	0.0395	10.59	1.56	2.03 ± 0.04
16	0.0395	10.02	2.08	1.93 ± 0.03
17	0.0395	12.30		2.51 ± 0.04
18	0.0395	9.73	2.34	1.85 ± 0.09
19	0.060	9.60		3.88 ± 0.07
20	0.030	8.64		1.30 ± 0.01
21	0.045	9.12		6.10 ± 0.15
22	0.030	9.60		2.98 ± 0.08
23	0.016	9.60		2.12 ± 0.07
24	0.045	9.60		2.99 ± 0.10
25[c]	0.0395	12.26		2.46 ± 0.03
26	0.0395	12.26		7.01 ± 0.19
27	0.0395	12.26		11.5 ± 0.01
28	0.0395	12.26		17.6 ± 0.8
29	0.0395	12.26		29.5 ± 0.4
30	0.0395	12.23		2.40 ± 0.09[a]
31	0.0395	12.23		2.16 ± 0.20
32	0.0395	12.23		2.12 ± 0.11[b]
33	0.0395	8.98	3.12	1.79 ± 0.23
34	0.0395	8.48	3.66	1.91 ± 0.04
35	0.0395	6.84	5.26	1.83 ± 0.06
36	0.0395	7.79	4.31	1.96 ± 0.04
37	0.0395	9.01	3.10	1.98 ± 0.04
38	0.0395	2.59	8.88	1.94 ± 0.09

[a] $[Mo(IV)] = 3.4 \times 10^{-4}$ M. [b] $[Mo(VI)] = 1.1 \times 10^{-4}$ M.
[c] For runs 25–29 T = 0.0, 10.0, 15.0, 20.0, and 25.0 °C, respectively.

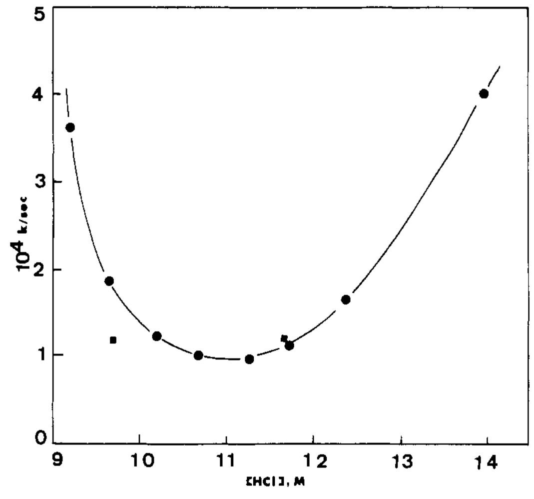

Figure 2. k_{obsd} vs. [HCl] for $[MoOCl_5]^{2-}$–H_2O exchange (0 °C; $[Mo]_t = 3.23 \times 10^{-2}$ M).

A graph of k_{obsd} vs. [HCl] at constant I (12.1–12.3 (LiCl)) showed nearly the same agreement with a [HCl] or $[HCl]^2$ term. The first-order term is considered to be the most reasonable when all of the data from 2–12 M HCl are considered. However,, a $[HCl]^2$ term is not ruled out primarily because the concentration range available is small and because at these high concentrations one cannot expect the kinetics to mirror

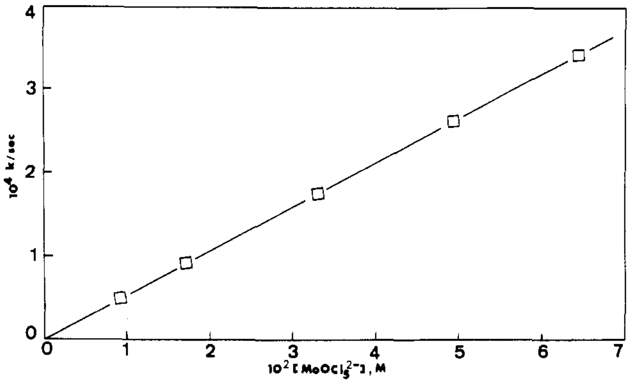

Figure 3. rate constants for $[MoOCl_5]^{2-}$–H_2O exchange (0 °C; [HCl] = 12.1 M).

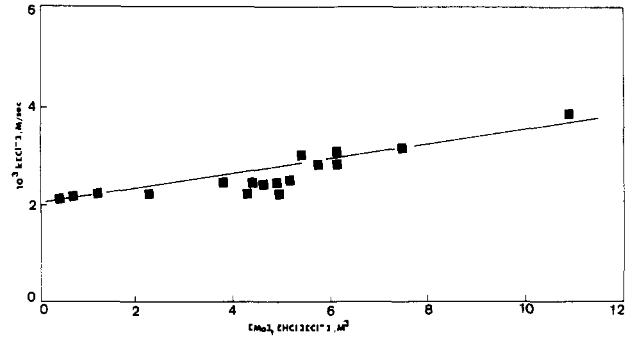

Figure 4. [HCl], [Cl^-], and [Mo(V)] dependence of rate constants for $[MoOCl_5]^{2-}$–H_2O exchange (0 °C; I = 12.1–12.3).

exactly the concentration changes due to molecule and ion-pair association and the low and changing concentration of solvent water. Since we have even less faith in H_0 values, we have chosen to explain the observations in terms of formal concentrations. While it may be subject to error, past experience suggests that it is the best choice. In the high-acidity region, 12.1–12.3 M, the $[Mo(V)]_t$ dependence was highly reproducible (Figure 3) and quite definitive. A straight line was obtained with a 2 ± 2 × 10^{-6} s^{-1} intercept, showing k_{obsd} to be a first-order function of $[Mo]_t$. Since $R = (k_{obsd}ab)/(a + b) = ka^nb^mc^p$—and b, $[H_2O]$, is much greater than a, $[[MoOCl_5]^{2-}]$—the rate law involving k has to have a term second order in $[[MoOCl_5]^{2-}]$ and, from the work described earlier, also first order in [HCl]. In the lower acidity region, [HCl] = 9.60 M, a similar straight line was observed (runs 19, 22, 23, 24) but with a large extrapolated intercept at $[[MoOCl_5]^{2-}]_t = 0$ of about (1.7 ± 0.1) × 10^{-4} s^{-1}. We interpret this result in terms of k_{obsd} having a zero- and first-order relationship with $[Mo(V)]_t$, the latter being a carry-over from the high-acidity region. Thus, in the low-acidity regions, the exchange equation is proportional to $[Mo(V)]^1$.

Runs 30 and 32 show that there is no appreciable effect on the rate constant if small quantities of $Mo_3O_4^{4+}$ or Mo(VI) (from MoO_4^{2-}) are present in the exchanging mixture. This is consistent with the reproducibility of k_{obsd} even though some oxidation by air probably takes place over the period of exchange study. It should be noted, however, that in the high-[Cl^-] solutions used no oxidation to Mo(VI) was ever observed.

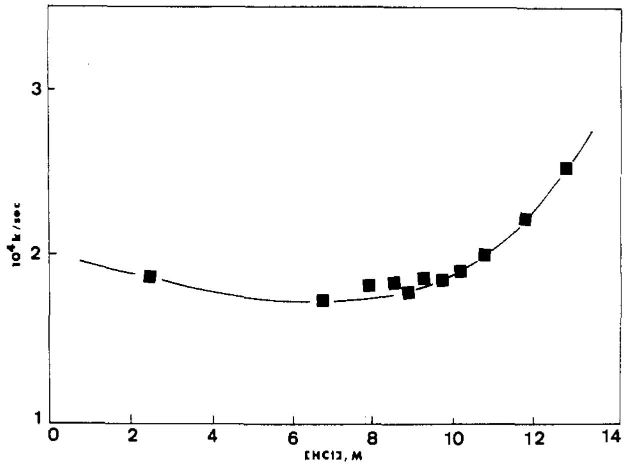

Figure 5. Acid dependence of oxygen-exchange rate constants for $[MoOCl_5]^{2-}$–H_2O (0 °C; I = 12.1–12.3).

Table III. Rate Constants of Oxygen Exchange for H_2O–$[MoOBr_5]^{2-}$ at 0 °C

[HBr], M	10^4 × $[[MoOBr_5]^{2-}]$, M	10^4k, s^{-1}
9.31	9.1	4.44 ± 0.05
9.36	18.9	7.78 ± 0.27
9.40	45.5	22.6 ± 1.1
7.94	18.9	68.5 ± 1.4

Using all the data at I = 12.1–12.3 (LiCl–HCl), an attempt was made to fit the data to the rate equation

$$R = k_{obsd}\left(\frac{ab}{a + b}\right) = k_1[[MoOCl_5]^{2-}]/[Cl^-] + k_2[[MoOCl_5]^{2-}]^2[HCl]$$

which can be rearranged to $k_{obsd}[Cl^-] = k_1 + k_2[[MoOCl_5]^{2-}][HCl][Cl^-]$. It follows that a graph of $k_{obsd}[Cl^-]$ vs. $[[MoOCl_5]^{2-}][HCl][Cl^-]$ should be linear. Figure 4 shows that all the data agree with this interpretation within the limits imposed by the variation in I. A similar plot can be constructed by utilizing the data at I = 9.6, but it is not nearly as definitive because of the small number of points and the larger scatter. A least-squares evaluation of both sets of data produced the following values for k_1 and k_2 at 0 °C (HCl–LiCl):

	I = 12.1–12.3	I = 9.4–9.6
10^2k_1, M s^{-1}	1.49 ± 0.15	1.64 ± 0.52
10^4k_2, M^{-2} s^{-1}	1.73 ± 0.33	3.74 ± 1.26

It appears that both k_1 and k_2 are sensibly constant within the experimental error. The reproducibility is limited mainly by the difficulty in maintaining the ionic strength at a constant value.

Figure 5 shows the results of studies at lower acidities while maintaining the [Cl^-] relatively high to prevent the formation of aquo species of MoO^{3+} and subsequent oligomerization. Since three solutions had to be mixed to give the final exchanging solution, it was not feasible to have I and $[[MoOCl_5]^{2-}]$ both constant. But it is clear that the rate of exchange reaches a limiting value in the lower acidity range in agreement with the form of the k_1 term given above. Even at very low acidities, e.g., ~2 M, the rate constant for exchange remains nearly constant, suggesting that acid–base hydrolysis is not very important.

With respect to this point, the vis–UV spectra of solutions of K_2MoOCl_5 in constant and high Cl^- concentration (I = 12.0) but with 2.0, 6.0, and 12.0 M HCl show practically no deviation from the molar absorption given earlier. Also, the IR spectra of solid samples of Cs_2MoOCl_5 obtained from the above solutions showed only the M=O stretching frequency at 940 cm^{-1} and no absorption due to coordinated or free H_2O, OH^-, or bridged O or OH.

The activation parameters were obtained from Figure 6 at [HCl] = 12.26 M and $[Mo]_t$ = 0.0395 M solutions. They are

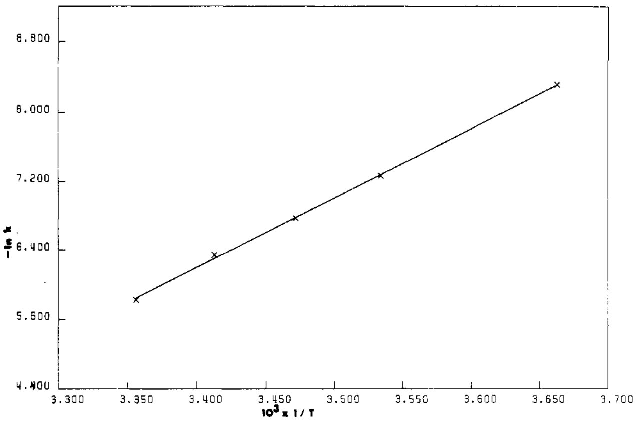

Figure 6. Temperature dependence of oxygen-exchange rate constants for $[MoOCl_5]^{2-}$–H_2O ($[Mo]_t = 0.0395$; $[HCl] = 12.26$ M).

$\Delta H^* = 64.2 \pm 0.2$ kJ/mol and $\Delta S^* = -78.1 \pm 0.2$ J/(mol K). In these runs the solutions were exactly the same, leading to the conclusion that the system is capable of very high precision when the solution composition can be accurately maintained.

Values for ^{18}O exchange H_2O and $[MoOBr_5]^{2-}$ are given in Table III. On the basis of these it can be said that the rate shows a second-order term in metal ion and an inverse dependence on [HBr] and is faster than that for $[MoOCl_5]^{2-}$.

Discussion

The results of the experiments described establish that the oxygen in the solid K_2MoOCl_5 is retained in solution and that it exchanges with solvent water with a half-time of hours at 0 °C.

The exchange rate, with a high-$[Cl^-]$ atmosphere to prevent aquation and maintain $[MoOCl_5]^{2-}$, follows the rate equation

$$R = k_1[[MoOCl_5]^{2-}]/[Cl^-] + k_2[[MoOCl_5]^{2-}]^2[HCl]$$

within reasonable limits of uncertainty from 2 to 14 M in HCl solution. In the high-acidity region, 9–14 M HCl where the k_2 term predominates, we suggest that protonation of the yl oxygen precedes dimerization through an yl oxygen, which results in oxygen exchange:

$$[Cl_5MoO]^{2-} + H^+ \xrightleftharpoons{K} [Cl_5MoOH]^-$$

$$[Cl_5MoOH]^- + [Cl_5MoO]^{2-} \underset{k_b}{\overset{k_{exch}}{\rightleftharpoons}} [Cl_5Mo{-}O{-}MoCl_5]^{2-} + OH^-$$

$$OH^- + H^+ \xrightleftharpoons{k} H_2O$$

If, as is likely, K is quite small and k_{exch}/k_b is also small, then $R = k_{exch}[Cl_5MoOH]^- [[Cl_5MoO]^{2-}] = kK[H^+][[MoOCl_5]^{2-}]^2$ and $k_2 = kK$.

There is ample evidence for protonation with certain dioxo metal complexes (i.e. $[Re(en)_2O_2]^+$,[13] $[Re(py)_4O_2]^+$,[14] $[Mo(CN)_4O_2]^{4-}$ [15]), and with others it has been shown that protonation is almost nonexistent ($[Os(en)_2O_2]^{2+}$ [16] $VO_2^+(aq)$[2]). But with the only other mono-yl ion, $VO^{2+}(aq)$, no direct evidence appears to exist for protonation (even in the oxygen-exchange kinetic studies). Note however that in those studies the acidities have never been in the 10 M region.

In the less acidic region the exchange is governed by the rate equation

$$R = k_1[MoOCl_5^{2-}]/[Cl^-]$$

It is reasonable to suggest that this term comes about through the aquo hydrolysis product:

$$[Cl_5MoO]^{2-} + H_2O \xrightleftharpoons{K} [Cl_4MoO(H_2O)]^- + Cl^-$$

$$H_2O + [Cl_4MoO(OH_2)]^- \xrightarrow{k} \text{exchange}$$

Thus, $R = k[[Cl_4MoO(OH_2)]^-] = kK[[Cl_5MoO]^{2-}]/[Cl^-]$ and $kK = k_1$.

The water in the aquo intermediate probably has to be in an equatorial position to be effective in facilitating exchange, and the intramolecular electronic rearrangement mechanism (IER)[17] is an attractive mechanistic possibility. The important step in this mechanism is the electronic rearrangement that exchanges the yl-oxo and aquo positions with H atom transfer and only slight M–O distance changes. While no definitive proof of this mechanism has ever been given, in either this case or others, it seems to rationalize the available experimental data rather well.

A comparison of the ^{18}O-exchange studies with the visible spectral[8,18] and magnetic susceptibility changes[6,7] accompanying HCl dilution of $[MoOCl_5]^{2-}$ solutions shows no inconsistencies. As noted by Haight, there are no appreciable spectral changes in the 11–13 M HCl region in agreement with the idea that the fraction of Mo(V) in either the $[Mo(OH)Cl_5]^-$ or $[Cl_5Mo{-}O{-}MoCl_5]^{2-}$ forms is very small.

Beginning at about 9 M HCl, significant spectral changes occur that are most pronounced between 4 and 6 M HCl and a decrease in magnetic susceptibility also occurs. This species change is also reflected in an increase in ^{18}O-exchange rates as would be predicted for the reactions

$$H_2O + [Cl_5MoO]^{2-} \rightleftharpoons [Cl_4(OH)Mo{-}O]^- + HCl \rightleftharpoons [Cl_4(O)Mo{-}O{-}Mo(O)Cl_4]^{2-}$$

However, the nature of the dimer is not secure and may be $[Cl_3Mo(O)(OH)_2Mo(O)Cl_3]^{2-}$ or $[Cl_3Mo(O)O_2Mo(O)Cl_3]^{4-}$. Below 3–4 M HCl, further spectral changes occur that give the well-known $Mo_2O_4^{2+}(aq)$ through hydrolysis of Cl^-.

The mechanism does not appear to change drastically if at all on going to $[MoOBr_5]^{2-}$. The faster rate probably reflects the weaker Mo–Br bond and greater hydrolysis under comparable solution conditions. This suggests that stronger ligands (i.e. SCN^-) or chelating ligands (i.e. edta type) would lower the rate of oxygen exchange.

In summary, the ^{18}O-exchange measurements in this paper suggest that $[Cl_5MoO]^{2-}$ can be protonated to a limited extent in concentrated HCl solutions and this form is responsible for an increase in exchange rate. In lower HCl concentrations Cl^- hydrolysis leads to $[Cl_4Mo(O)(OH_2)]^{2-}$, which probably exchanges by the IER mechanism. When the $[Cl^-]$ is large but [HCl] small, little Cl^- hydrolysis occurs, preventing dimer formation, and the solutions exhibit a slow acid-independent oxygen-exchange rate. $[MoOCl_5]^{2-}$ and $[MoOBr_5]^{2-}$ show similar kinetic behavior.

With solutions of pH 2–5 and low $[Cl^-]$, $Mo_2O_4^{2+}(aq)$ is the predominate species showing two types of oxygen exchange rates (yl fast, bridging slow), and in more basic media further polymerization occurs, resulting in a gelatinous "hydroxide",

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(13) Kriege, L. B.; Murmann, R. K. *J. Am. Chem. Soc.* **1972**, *94*, 4557.
(14) Murmann, R. K. *J. Am. Chem. Soc.* **1971**, *93*, 4184.
(15) Murmann, R. K.; Robinson, P. R. *Inorg. Chem.* **1975**, *14*, 203.
(16) Malin, J.; Schlemper, E. O.; Murmann, R. K. *Inorg. Chem.* **1977**, *16*, 615.
(17) Rahmoeller, K. M.; Murmann, R. K. *Inorg. Chem.* **1983**, *22*, 1072.
(18) Bergh, A. A.; Haight, G. P., Jr. *Inorg. Chem.* **1969**, *8*, 189.

which still retains some of the bridging and yl oxygens unexchanged.

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Chlorotellurate(IV) Equilibria in Aqueous Hydrochloric Acid

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Study of TeO_2 in solutions of hydrochloric acid by UV-visible and Raman spectroscopy shows that three Te(IV) chloro anions are present: $TeCl_6^{2-}$, $Te(OH)Cl_4^-$, and a monochlorotellurate(IV) of probable composition $TeCl(OH)_4^-$. The compound $Me_4N[Te(OH)Cl_4]$ has been prepared and characterized by Raman and IR spectroscopy.

Introduction

Both the hexa- and pentachlorotellurate(IV) anions are well-known in the literature.[1,2] On the basis of Raman spectral studies it has been suggested that these ions may be present in solution of tellurium dioxide in aqueous hydrochloric acid.[3] While there is little doubt that $TeCl_6^{2-}$ is formed in concentrated hydrochloric acid, the nature of other Te(IV) species in more dilute HCl solutions is not precisely known. Polarographic[4] and solvent-extraction[5] studies have been interpreted in terms of a complete range of anions with Cl/Te ratios from 1 to 6 and varying degrees of solvation. Selenium dioxide forms selenious acid, seleninyl chloride, and the pentachloroselenate(IV) ion in hydrochloric acid solutions while the hexachloroselenate(IV) ion is apparently not a major constituent.[6] In concentrated hydrofluoric acid, the pentafluoro- and tetrafluorohydroxotellurate(IV) ions are found.[7] The crystal structure of tetraphenylarsonium aquotetrachlorohydroxotellurate(IV) has been determined.[8] However, it is uncertain as to whether the anion in this compound is $TeOCl_4^{2-}$ or $Te(OH)Cl_4^-$. In order to help answer this question as well as to extend our study of halochalcogenate(IV) species formed in hydrochloric acid, we undertook a Raman and UV-visible spectroscopic study of this system.

Experimental Section

Hydrochloric acid and tetramethylammonium chloride were from J. T. Baker, and tellurium dioxide was from Matheson Coleman and Bell. All chemicals were analyzed for purity before use.

Tetramethylammonium tetrachlorohydroxotellurate(IV) was prepared on a gram scale by mixing together a 1/1/3 mole ratio of $Me_4NCl/TeO_2/HCl$ (as 8 M HCl). The mixture was ground together, left to stand for 1 day, and then filtered. The yellow-green product was washed with cold ethanol and ether and stored in a vacuum desiccator out of light, which caused darkening over a period of days. Anal. Calcd for $Me_4N[Te(OH)Cl_4]$: Cl, 39.33. Found: Cl, 39.38. Similar preparations using NH_4Cl and CsCl in place of Me_4NCl gave mixtures of TeO_2 and the hexachlorotellurate(IV). Attempted preparation of tetramethylammonium chlorotellurate(IV) by similar procedures (1/1 mixture of Me_4NCl and TeO_2 in minimum water) yielded only insoluble TeO_2.

Table I. Spectrophotometric Results for Solutions of 0.001 M TeO_2 in Moderately Concentrated HCl (c_{HCl} = 7.00-8.50 M)

c_{HCl}, M	A_{375}	$10^4 \times [TeCl_6^{2-}]$, M	$10^4 \times [TeCl_x]$, M	a_{HCl}[a]	a_{H_2O}[b]
8.50	0.276	9.06	0.94	129	0.380
8.00	0.250	8.26	1.74	97.5	0.422
7.50	0.228	6.99	3.01	73.0	0.466
7.00	0.193	5.54	4.46	56.0	0.510

[a] Reference 11. [b] Mole fraction scale.[12]

Analysis of starting materials and $Me_4N[Te(OH)Cl_4]$ was by Volhard titration for chloride, by permanganimetric titration for Te(IV) (in TeO_2), and against sodium carbonate using bromocresol green for HCl concentration.

Spectrophotometric and Raman spectral measurements were carried out as described previously.[6,9] All spectra were measured at 25 °C. All absorbances were corrected for HCl background. $Me_4N[Te(OH)Cl_4]$ was readily pyrolyzed by the laser light at 647.1 nm, and the spectra had to be run at low power levels.

Results and Discussion

The spectrophotometric measurements on 0.001 M TeO_2 solutions in the ranges 7.0-10.0 M HCl and 3.0-5.0 M HCl are shown in Figure 1A,B, respectively. Correspondingly, the Raman spectra of 0.5 M TeO_2 solutions in 3.0-11.0 M HCl are shown in Figure 2. The UV-visible and Raman spectra of TeO_2 in the most concentrated HCl solutions (10.0-11.8 M) are due to the $TeCl_6^{2-}$ ion.[3,10] As the concentration of HCl is decreased to 7.0 M, the peaks in the UV-visible spectra at 268 and 375 nm due to $TeCl_6^{2-}$ fall in intensity and are replaced by peaks at 295, 253, and 225 nm. Isosbestic points occur at 235 and 255 nm. Over this concentration range an equilibrium between $TeCl_6^{2-}$ and a second Te(IV) species is established, and this is confirmed by matrix-rank plots.[11] The concentration of $TeCl_6^{2-}$ may be determined from the absorbance at 375 nm by using the extinction coefficient of

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(1) Beattie, I. R.; Chudzynska, H. *J. Chem. Soc. A* **1967**, 984.
(2) Creighton, J. A.; Green, J. H. S. *J. Chem. Soc. A* **1968**, 808.
(3) Hendra, P. J.; Jovic, Z. *J. Chem. Soc. A* **1968**, 600.
(4) Simao, J. E.; Veiga, A. S. *Rev. Port. Quim.* **1974**, *16*, 129.
(5) Iofa, B. Z.; Wang, W.-H.; Ridvan, M. R. *Radiokhimiya* **1966**, *8*, 14.
(6) Milne, J.; Lahaie, P. *Inorg. Chem.* **1979**, *18*, 3180.
(7) Milne, J. B.; Moffett, D. *Inorg. Chem.* **1974**, *13*, 2750.
(8) Collins, P. H.; Webster, M. *J. Chem. Soc., Dalton Trans.* **1974**, 1545.
(9) Mahadeevan, M.; Milne, J. B. *Inorg. Chem.* **1983**, *22*, 1648.
(10) Couch, D. A.; Wilkins, C. J.; Rossman, G. R.; Gray, H. B. *J. Am. Chem. Soc.* **1970**, 92, 307.
(11) Coleman, J. S.; Varga, L. P.; Mastin, S. H. *Inorg. Chem.* **1970**, *9*, 1015.