ReO_4^-–H_2O Exchange Kinetics in Methanol Using Oxygen-18

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Abstract: The ^{18}O exchange between ReO_4^- and H_2O has been studied in methanol solution. The kinetic expressions are basically the same as those with water as a solvent. In methanol the rate is relatively insensitive to $[H_2O]$ in the neutral and acidic regions. This suggests that the mechanism of oxygen exchange is closer to a dissociation facilitated by solvent hydrogen bonding than a displacement. Isotope fractionation factors are also presented.

Considerable interest has been shown over an extended period of time in the mechanism of oxygen atom exchange between water and oxyanions of the type MO_4^{n-} and oxy species with fewer than four equivalent oxygens.[1] Much of this interest stems from oxidation–reduction atom-transfer experiments which usually require a qualitative knowledge of the kinetics of the exchange process. However, an equally important aspect is the fundamental mechanism(s) which governs the process and whether a general mechanism exists for certain geometries, *i.e.*, tetrahedral oxyanions.

This paper reports results of experiments designed to provide information about the mechanism of H_2O–ReO_4^- exchange. For this and many similar oxyanions the rate law is known[2] to have the form rate/MO_4^{n-} = $k_0 + k_H[H^+]^2 + k_{OH}[OH^-]$, where one or more of the terms may be small and not observed. The order with respect to water (which is usually the solvent) has not been determined since the water concentration usually cannot be varied without a major change in the bulk properties of the solvent and their concurrent effects. The perrhenate ion, which has been shown to be tetrahedral in solution,[3] has unique properties which allow nearly anhydrous MeOH to be used as a solvent, with traces of water being present as one of the reactants. The important properties are high solubility, a relatively rapid exchange rate so high temperatures can be avoided, the weakness of ReO_4^- as a base so acid–base dissociation constants are not involved, and its nonoxidizing tendencies which avoid solvent reaction. Further it will be shown that both CH_3OH–H_2O exchange and ReO_4^-–CH_3OH oxygen exchange are infinitely slow compared to the reaction being studied, namely the ReO_4^-–H_2O oxygen exchange.

Experimental Section

Materials. $NaReO_4$ was prepared as previously described[2] and recrystallized from water, taking the middle third fraction. Water was distilled from acid CrO_3, basic $KMnO_4$ solution, and then by itself. In the early experiments, the ReO_4^- was enriched in ^{18}O ($\cong$2.5 times normal enrichment), while the bulk of the measurements were carried out with enriched water. The results were equivalent. The ReO_4^- was enriched by equilibration with ^{18}O water for several weeks at room temperature. It was recrystallized and dried at 60° under 10^{-4}–10^{-5} mm of pressure. Methanol was of AR anhydrous grade and was refluxed with Mg metal until $Me(OMe)_2$ was formed. It was then slowly distilled in a closed, all-glass apparatus, taking special care that no $Mg(OMe)_2$ was carried over and that no water was absorbed. Even with these precautions, some water was present in the purified MeOH. This was determined by vapor-phase chromatography using a Porapack column at 60°. Standardization of the detector response was done by measuring methanol samples containing known amounts of added water. The amount of water present in MeOH was also determined in each kinetic run by isotopic dilution. Using the zero and infinite values of the ^{18}O content of ReO_4^- the total water content of the solution was calculated which was compared with the amount of water added. For the solutions where small amounts of water were added, the agreement between this method and the vpc method was excellent. In the other cases less accurate results were obtained by isotopic dilution since the solvent water concentration was the difference between two large concentration terms.

Isotopic Measurement. A description of the isotopic measurements used has been given previously.[2] They consisted of precipitating $CsReO_4$, converting it to CO_2, purifying the CO_2 by vpc, and measuring the 46/(44 + 46) ratio on a Nuclide double-collector RMS-16 mass spectrometer. All reported values are normalized to 2.00×10^{-3} for a standard, normal CO_2 sample.

ReO_4^-–H_2O Exchange. Neutral Region. About 0.10 g ± 0.02 mg of $NaReO_4$ (normal) was dissolved in 20 ml of anhydrous methanol contained in a water-jacketed cell of 25-ml volume. The water flowing in the outer compartment was thermostated and held its contents at a measured 25.00 ± 0.02°. Emphasis was placed on long-term stability. Laboratory light was excluded with a covering of tin foil. At time zero, 5–200 μl of water, about 8.3 times normal ^{18}O content enriched, was added with shaking, and additional absolute methanol was added to the 25.0-ml mark. The vessel was sealed between samples with a Teflon stopper and covered with a paraffin-coated plastic. At timed intervals, 2-ml samples were withdrawn into a cooled (0°) test tube containing 0.2 ml of a nearly saturated $CsCl$–H_2O solution. After about 3 min at 0° the $CsReO_4$(s) was collected on a sintered-glass filter, washed with absolute MeOH and acetone, and dried for 4 hr over anhydrous $CaSO_4$. It was then dried under high vacuum and converted to CO_2 for isotopic measurement. All glassware was dried at 250° for 2 hr and stored in a desiccator. Solution makeup and sample collection were carried out in a laboratory held at 25 ± 1° and with about 10–25% humidity. No effect could be noticed due to water pickup during the initial solution preparation or while taking the seven 2-ml samples, as judged by vpc and by the infinite value from the kinetic runs. Special care was taken to minimize atmospheric contamination during the long-period samples.

In the neutral region the half-time for exchange is about 3000 hr, which prevented following a large portion of the reaction. The decision not to use elevated temperatures was made early in the study. The major disadvantages of an elevated temperature, say 50°, are the likelihood of evaporative losses and the increased possibility of contamination by water during sampling and during the timed intervals. At least seven samples were taken for each kinetic run spanning a time interval of 170 to 330 hr. A typical plot is given in Figure 1. The infinite value was obtained by adding 1 μl of concentrated HCl to 2 ml of the solution, waiting 8 hr for equilibration, and precipitating $CsReO_4$ in the usual manner. The water added with the acid was taken into account in the calculation of the infinite value.

ReO_4^-–H_2O Exchange. Acid Region. The initial experiments were conducted by injecting $NaRe^{18}O_4$ into mixtures of HCl and

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(1) A. G. Sykes, "Kinetics of Inorganic Reactions," Pergamon Press, New York, N. Y., 1966, p 269.
(2) R. K. Murmann, *J. Phys. Chem.*, 71, 974 (1967).
(3) R. H. Busey and O. L. Keller, Jr., *J. Chem. Phys.*, **41**, 215 (1964).

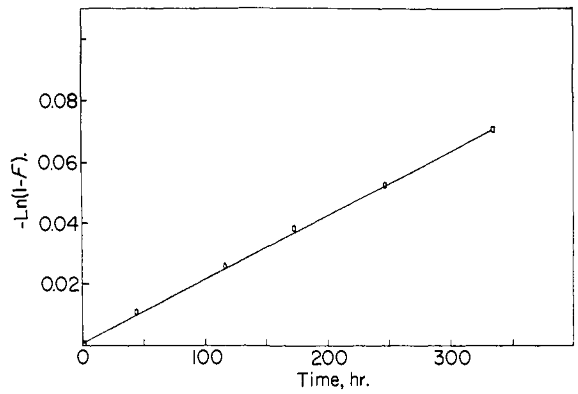


Figure 1. ReO_4^--H_2O exchange in methanol at 25°, $[ReO_4^-] = 0.02005$, $[H_2O] = 0.0111$; neutral region.

H_2O in methanol in a constant-temperature water bath. At measured intervals, portions were neutralized at 0° and the $CsReO_4$ was precipitated and analyzed. Differing results were obtained when freshly prepared solutions of normal $NaReO_4$, $H_2{}^{18}O$, and MeOH were used, with initiation being the addition of HCl. In the former the rate of reaction decreased in direct relation to the length of time the acid was in contact with the alcohol (Table III). This suggested that the acid was slowly being consumed, forming CH_3Cl. This was subsequently verified by vpc using known synthetic CH_3Cl samples. The rate of oxygen exchange was considerably faster than the loss of acid, however, and when the acid was added to initiate the reaction (the nonacid ^{18}O exchange term is very small by comparison), the loss of acid over the period of exchange followed (0-80%) was less than 2%. Thus linear McKay graphs were obtained.

The slope of graphs of $-\ln(1 - F)$ *vs.* time gave k_{obsd}, which is related to R (mol of exchangeable O $l.^{-1}$ sec^{-1}) by the equation

$$R = k_{obsd}\left(\frac{4[ReO_4^-][H_2O]}{4[ReO_4^-] + [H_2O]}\right)$$

All observed rate constants were obtained by a weighted least-squares analysis of the data and ± values listed are one standard deviation.

Table I. ReO_4^--H_2O Exchange (Neutral, 25°)

$[ReO_4^-] \times 10^2$	$[H_2O]^b \times 10^2$	k_{obsd}, hr^{-1}, $\times 10^4$	R, M sec^{-1}, $\times 10^9$
		In Methanol[a]	
2.01	2.22	1.016 ± 0.060[c]	0.491
2.61	4.44	1.109 ± 0.046	0.960
2.25	11.12	0.698 ± 0.035	0.964
3.15	17.77	1.167 ± 0.031	2.388
2.46	22.22	1.091 ± 0.070	2.065
2.83	30.21	1.374 ± 0.032	3.141
3.07	14.01	1.149 ± 0.027	2.088
2.791	5.56	1.530 ± 0.019	1.576
4.317	6.67	1.745 ± 0.017	2.331
4.263	22.22	2.102 ± 0.046	5.633
1.643	11.12	0.771 ± 0.030	0.884
2.005	1.11	2.104 ± 0.026	0.571
		In H_2O[a]	
5.361		7.74 ± 0.22	4.59
2.878		6.90 ± 0.16	2.20
1.797		7.12 ± 0.05	1.420

[a] All carried out in darkness. [b] Calculated from H_2O added + methanol-water. [c] ± values are for one standard deviation.

Fractionation Factor, $[NaReO_4]$ and $[Re(py)_4O_2]ClO_4$. Water solutions (25 ml) of $NaReO_4$ (8.38×10^{-2} M) and $[Re(py)_4O_2]ClO_4$ (4.35×10^{-3} M) were equilibrated at 25.0° in a water bath. Samples were precipitated ($CsReO_4$ and $[Re(py)_4O_2][Cr(NH_3)_2(SCN)_4]$) after 1 month and again after 1.5 months of equilibration time. Both precipitations were very rapid and nearly quantitative and the products nonhydrated. The solids were collected and carefully dried and the contained oxygen was converted to CO_2 in a sealed tube using $Hg(CN)_2$ at 425°. Isotope ratio measurements were made utilizing the dual-inlet system with corrections for valve leakage (<1%).

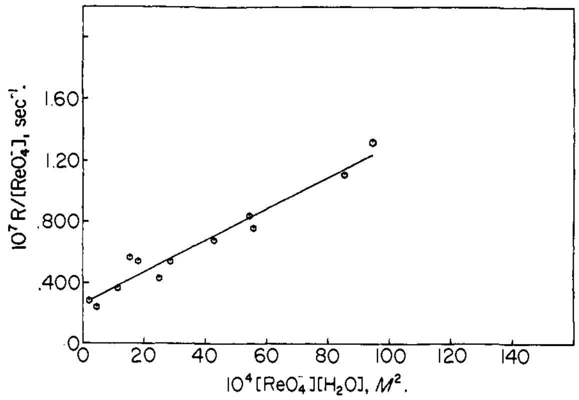


Figure 2. Exchange data in the form of the equation $R = k[ReO_4^-] + k'[ReO_4^-]^2[H_2O]$.

Results

A representative example of a rate determination is given in Figure 1. The results for the neutral region are tabulated in Table I. The question of whether MeOH exchanges with ReO_4^- or H_2O is settled by Table II. It does not, in the time interval used. Numerous attempts to fit these results to a rate equation involving $[ReO_4^-]$ and H_2O lead to the "best fit" by the equation $R = k[ReO_4^-] + k'[ReO_4^-]^2[H_2O]$. This is shown in Figure 2. In Table III are listed the results of experiments in the acid region. The rate is essentially second order in $[H^+]$ or $[HX]$ and first order in $[ReO_4^-]$ and shows essentially no dependence on $[H_2O]$. Table IV lists the results of isotopic fractionation between two Re oxyanions and water.

Table II. Nonexchange of MeOH Oxygens[a] with H_2O-ReO_4^-; Neutral

Time of contact, hr	$N_{H_2O(initial)}$
165	0.030458
165	0.032535
175	0.032249
186	0.033640
186	0.033117
	Av 0.032399[b]

[a] $H_2{}^{18}O$ added to ReO_4^- in MeOH. The initial ^{18}O content of H_2O was calculated from the amounts of H_2O and ReO_4^- added and the final ^{18}O content of $CsReO_4$, assuming no exchange with MeOH. [b] This value should be 0.03308. The slightly lower value obtained comes from traces of water in the alcohol. If exchange with MeOH occurred and were complete, this value would be 0.00407.

Discussion

On the basis of the amounts of reactants, their ^{18}O enrichment, and the final enrichment in $CsReO_4$ there is no ^{18}O-water exchange with methanol under the concentration and time conditions used in this study. Table II points this out in the neutral region, and a similar set of data was collected in the acid region. The experimental precision was ample for demonstrating the main features of the mechanism but is not reliable enough to distinguish between rate expressions

Table III. ReO_4^-–H_2O Exchange in MeOH; Acid Region, 25° (HCl)

$[ReO_4^-]$	$[H_2O]$	MeOH–HCl[a] contact time, min	$t_{1/2}$, sec	$10^3[H^+]_{initial}$	$10^{-4}k''$
0.0300	0.585	60	33	1.20	4.80[c]
0.0310	0.585	1440	68	1.20	2.32
0.0310	1.030	3620	144	1.20	1.20
$[ReO_4^-]$[b]	$[H_2O]$		$t_{1/2}$, sec	$10^3[H^+]$	$10^{-4}k''$
0.0208	0.1131		114	0.446	7.04
0.0212	0.0242		40	0.446	7.72
0.0240	0.1131		77	0.446	9.56
0.0238	0.0505		20	0.803	7.40
0.0245	0.0505		169	0.251	8.84

[a] During this time some MeOH–HCl reaction occurred which deleted the total acid present. [b] In this set freshly prepared HCl–MeOH and MeOH–$H_2{}^{18}O$–ReO_4^- solutions were mixed to initiate the reaction. [c] $k'' = 4(0.693)[H_2O]/t_{1/2}(4[ReO_4^-] + [H_2O])[H^+]^2\ M^{-2}\ sec^{-1}$.

Table IV. ^{18}O Fractionation between ReO_4^- and H_2O[a]

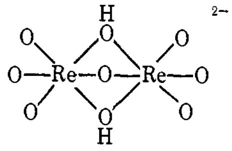
H_2O–$NaReO_4$, 25°, $M = 0.084$		
$[ReO_4^-/H_2O]$ ^{18}O ratio	1.01074	1.00997
	1.01063	1.00999
	1.01050	
	Av 1.01037 ± 0.00024[b]	
H_2O–$[Re(py)_4O_2]^+$, 25°, $M = 4.35 \times 10^{-3}$		
$[[Re(py)_4O_2]^+/H_2O]$ ^{18}O ratio	1.01274	

[a] Results constant after 1 month. Data for 1- and 1.5-month equilibration times. [b] Standard deviation.

differing only slightly. The isotopic fractionation factor is small enough to be neglected even though only a portion of the exchange was measured.

Neutral Region. The main feature is the rather minor effect that $[H_2O]$ has on R. The first term, $k[ReO_4^-]$, appears to be well demonstrated and may be directly compared with that measured in water.[2] The two values are, for water, $8.03 \pm 0.40 \times 10^{-8}$ sec^{-1} and, for methanol, $2.59 \pm 0.37 \times 10^{-8}$ sec^{-1}. (In 0.1 M LiCl[2] this value was 7.83×10^{-7} sec^{-1} after removal of the assumed water term.) The factor of ~3 increase in rate with the solvent water may be a consequence of the small increase in acidity $CH_3OH \rightarrow H_2O$[4] or to the increase in dielectric constant of the medium. The significance of the former relationship may be quite important since water cannot play a much more specific role without entering into the rate equation. Thus, a tentative mechanistic description would suggest an activated state on the side of oxygen ion dissociation facilitated by general hydrogen bonding using both MeOH and H_2O. This picture requires that CH_3OH satisfactorily compete with water for hydrogen-bonding positions on ReO_4^- in the concentration region studied and that, as the rhenium oxygen is released, sufficient water be available to complete the exchange.

The form of the second term, $k'[ReO_4^-]^2[H_2O]$, is not unambiguously settled. Because of its complexity and the scatter in the data, some other rate laws might more correctly describe the system. However, this form is not unreasonable and would be consistent with the formation of



in trace concentrations leading, upon dissociation, to oxygen exchange. The value of k' is $1.037 \pm 0.78 \times 10^{-5}$ M^{-2} sec^{-1} at 25°.

Acidic Region. The rate retains its second-order term in H^+ or HX and shows no water dependence. A value of k'' of 8.12×10^4 M^{-2} sec^{-1} in MeOH can be compared to that previously obtained[2] in 0.1 M LiCl–H_2O solution (1.86×10^3 M^{-2} sec^{-1}). Numerous reasons for this difference could be cited, but no means of differentiating between them is available. This rate expression suggests that the reacting aggregate has a considerably weakened Re–O bond before the solvent interaction becomes important in carrying the exchange to completion. Like the first-order term in the neutral region, either sufficient water must be present in the vicinity of the distorted ReO_4^- to prevent reincorporation or MeOH can temporarily take a coordination position on the rhenium and be later replaced by water. In either case a water-dependent term would become apparent if water had to compete with the original oxygen for the vacated coordination position. A distinction between these two alternatives cannot be made with any available experimental results.

Of value would be studies in other organic solvents of differing acidity and the temperature dependences. It is expected that future studies will be along these lines.

The conclusion of this first study of the water dependence of an $^{18}OH_2$ exchange with a tetrahedral oxyanion is that exchange is facilitated by hydrogen bonding to proton "showing" solvents or by association with $2H^+_{solvated}$.

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