Inorg. Chem. **1999,** *38,* 3919−3921

Oxygen Exchange on ReO_4^- and TcO_4^- by ^{17}O-NMR

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Received March 12, 1999

The kinetics of oxygen exchange between TcO_4^- and solvent water has been examined at 25 °C using ^{17}O NMR measurements. The data suggest the rate equation $k_{obs} = k_H[H^+]^2 + k_0$. The rate constant for the $[TcO_4^-][H^+]^2$ term is 32.6 M^{-2} s^{-1}, which is a factor of 2 smaller than that for ReO_4^-. Oxygen exchange with solvent water at neutral pH is extremely slow for both TcO_4^- and ReO_4^- with the acid independent rate constants being 5×10^{-9} M^{-1} s^{-1} and 1.4×10^{-8} M^{-1} s^{-1}, respectively. In the presence of the complexing citrate ion the ReO_4^-−H_2O exchange is dramatically increased in the acid independent region, but this ligand has little effect on TcO_4^-. This suggests that ReO_4^-, but not TcO_4^-, is capable of expanding its coordination number. In agreement with this concept of coordination number expansion, there is no significant $[OH^-]$ dependent term in the rate law for TcO_4^-, as there is for ReO_4^-.

Introduction

There are relatively few reports in which the kinetics of analogous technetium and rhenium compounds have been investigated. Part of this stems from the fact that all isotopes of technetium are radioactive, making its handling difficult. These comparisons are valuable for a fundamental understanding of periodic trends and especially since rhenium is often used as a nonradioactive chemical analogue for technetium. Interest in the chemistry of technetium derives mainly from the importance of the isotope Tc-99m in diagnostic nuclear medicine and of Tc-99 in nuclear waste sites and as a potential environmental contaminant.[1−4] The chemical form of technetium most readily available, the pertechnetate oxoanion, is obtained both from a Mo-99/Tc-99m generator for nuclear medicine applications and as the Tc-99 fission product from U-235 and Pu-239 reprocessing.

Several reports in the literature suggest that pertechnetate and perrhenate behave differently under conditions in which their structural similarities (virtually superimposable crystal structures because of the lanthanide contraction) would not have predicted such differences. These differences have been suggested to arise from the ability of perrhenate ion, but not pertechnetate ion, to expand its coordination number above 4 by ligand incorporation. In one report, pertechnetate and perrhenate ions were separated by reversed-phase HPLC by the addition of 0.01 M citrate in the mobile phase. Citrate bound to perrhenate but not (or much less) to pertechnetate, resulting in the retention of the rhenium.[5] Vajo showed that the electroreduction of perrhenate in the presence of citrate or oxalate indicated the formation of complexes with perrhenate that were postulated to be 6 coordinate.[6] Deutsch showed that biological handling of $^{99m}TcO_4^-$ and $^{188}ReO_4^-$ in mice was quite different, with the pertechnetate concentration in all tissues sampled being significantly higher than the perrhenate concentration. Deutsch suggests that this indicates a more efficient renal clearance pathway for rhenium possibly through a 6-coordinate Re(VII) species.[5]

To investigate the differences in the ability of pertechnetate and perrhenate to expand their coordination numbers, we undertook a study to directly compare oxygen exchange kinetics over a wide pH range and in the presence of citrate ion. The rate of oxygen exchange for perrhenate ion has been previously measured over an extended pH range by using mass spectrometric methods.[7−10] The rate equation for the exchange between water and perrhenate ion has an acid dependent term, a hydroxide dependent term, and a pH independent term.[7,8] The expression given[7,8] for the exchange at 25 °C is

$$\text{rate} = k_0[H_2O][ReO_4^-] + k_{2H}[H_2O][ReO_4^-][H^+]^2 + k_{OH}[H_2O][ReO_4^-][OH^-]$$

where $k_0 = 1.4 \times 10^{-8}$ M^{-1} s^{-1}, $k_{2H} = 33.6$ M^{-3} s^{-1}, and $k_{OH} = 1.55 \times 10^{-4}$ M^{-2} s^{-1}.

In another study by mass spectrometry, a more limited comparison of the rates of oxygen exchange on pertechnetate and perrhenate ions was made[11,12] under acidic conditions (pH < 4) where both atom types followed the rate equation

$$\text{rate} = k[H_2O][MO_4^-][H^+]^2$$

which is consistent with Murmann's findings[7−9] in the acidic

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10.1021/ic9902830 CCC: $18.00

region ($k = 2.0$ M^{-3} s^{-1} for pertechnetate and 49.2 M^{-3} s^{-1} for perrhenate).

In this study, the oxygen exchange between pertechnetate and water is determined using ^{17}O NMR spectroscopy in the acidic, neutral, and basic pH regions. The effect of citrate ion on the oxygen exchange was also measured. Perrhenate ion was studied to validate our use of the NMR method of kinetic oxygen transfer measurement using a nonradioactive ion. The rate constants for oxygen exchange on pertechnetate and perrhenate ions are compared.

Experimental Section

CAUTION! Tc-99 is a low-energy β emitter with a half-life of 2.1 × 10^5 years. Appropriate radiation safety procedures were used at all times by personnel trained in the safe handling of radioactivity.

Materials. $NH_4{}^{99}TcO_4$ was obtained from Oak Ridge National Laboratory or as a gift from Mallinckrodt Medical, Inc., in St. Louis. $KTcO_4$ was prepared by addition of a stoichiometric quantity of KOH to an aqueous solution of NH_4TcO_4 and removal of the NH_3 and solvent under vacuum. Recrystallization from water yielded the desired salt on slow evaporation. ^{17}O-Enriched water (20.1%) was obtained from Isotec (Johnson-Matthey); it was also 18.1% enriched in ^{18}O. All other chemicals were reagent grade and used as received unless otherwise specified. Solvent water was deionized and then distilled.

Preparation of ^{17}O-Enriched MO_4^-. $NaReO_4$ and $KTcO_4$ were enriched in ^{17}O using the following procedure. Solutions of purified $NaReO_4$ or $KTcO_4$ (ca. 75 mg, 0.5 mL) were dried in a vacuum system capable of better than 10^{-3} mmHg. About 0.3−0.5 mL of ^{17}O-enriched water was added, and a measured amount of 10^{-2} M sulfuric acid (ca. 1−5 μL) was added. The solutions were allowed to equilibrate at room temperature overnight or longer, and then the requisite amount of dilute NaOH solution was added to reach neutrality. Qualitatively, the exchange was found to be complete. Buffers were not generally employed because of their potential for affecting the rate of the reaction. The enriched water was removed, without significant heating, at a temperature below 25 °C under vacuum until dry and the recovered water was retained for use in the next run.

NMR Experiments. Solutions were prepared using distilled water having the requisite amount of acid or base which, when added to the solid pertechnetate or perrhenate salt, would approximately yield the desired pH. The solution was held in a thermostated water bath. About 1 mg of a sample of ^{17}O-enriched sulfate ion was added as an internal standard. The solid ^{17}O-enriched pertechnetate or perrhenate salt (about 10 mg) and the internal standard were dissolved in 1.0 mL of water. About 0.5 mL of this solution was placed in a 5.0 mm glass NMR tube (for ReO_4^-) or a Teflon inner sleeve (∼2.5 mm) contained in a 5.0 mm glass NMR tube (for TcO_4^-). Sodium citrate (solid) was added to make the resultant solution 0.10 M in citrate ion in experiments involving the effect of citrate ion on the observed rate. After sealing and stirring, the tube was placed in a Bruker 500 MHz NMR instrument at the desired temperature. The intensity and the peak height of the ^{17}O peak(s) were measured as a function of time using the sulfate ion peak as a standard. The first measurement was not on the line of the other points but differed slightly presumably due to small temperature changes which occurred during transfer. In all cases (unless mentioned otherwise) an infinity value was obtained which was quite small and agreed with the calculated value. The pH of the final solution was measured after the NMR experiments were complete using a pH meter and buffer-standardized 1 mm diameter electrodes.

The ^{17}O NMR spectrum contained resonance peaks due to water (set to 0.0 ppm), the sulfate (165.1 ppm), and a one-line ReO_4^- signal at 561.1 ppm or a 10-line TcO_4^- multiplet arising from the $I = 9/2$ for Tc-99 centered at 749.7 ppm ($J = 1.94$ ppm).[13−16] All resonances were downfield of $H_2{}^{17}O$. The intensity of the sulfate ion peak remained nearly constant with time and was used as an internal standard for integration.[17] The MO_4^- peak decreased with time, and the water peak increased as the exchange occurred. Either the MO_4^- oxygen signal(s) or the water oxygen resonance could have been used for the rate determination, but while they agreed qualitatively, the MO_4^- oxygen peak gave the most precise and consistent rate constants. Near time zero, the water peak was quite small as expected from the known nonhydrate nature of the chosen MO_4^- salts. The number of NMR scans per timed measurement was varied between about 100 and 300 with the time of data collection usually being less than 5% of the half-time for exchange.

Results and Discussion

The integrated intensities of the peak(s) for ^{17}O in MO_4^- were measured as a function of time and compared to that of SO_4^{2-} which was also present in each sample. SO_4^{2-} exchanges its oxygen with solvent water at an extremely slow rate.[17−19] At the acidities employed, there was effectively no change in the $S^{17}O_4^{2-}$ content even with samples equilibrated over many weeks. A graph containing both Tc and Re experiments is given in the Supporting Information. At least six and usually 10 points were taken for each run, with the first point being discarded or given a small weight. The infinite values (about 2% of the initial) measured after about 10 half-times agreed within experimental errors with those calculated. In the alkaline region for TcO_4^-, the infinite value was calculated because of the excessively long half-times under those conditions. All least-squares graphs of $\ln(1 - F)$ (where F = the fraction reacted) versus time were linear with correlation coefficients, R, of about 0.99. The rate constant, k_{obs}, was obtained from the nonweighted least-squares slopes of these graphs. Weighting of the individual points was not done because the predominate error appeared to be associated with the reproducibility of the NMR measurements and did not appear to be related to the magnitude of the value of $\ln(1 - F)$.

The first experiment for ReO_4^- at a pH of 9.0 gave a k_{obs} value of 4.9×10^{-7} s^{-1} at $\mu = 0.3$, compared to the earlier value of 2.97×10^{-7} s^{-1} at $\mu = 0.1$ calculated from the ^{18}O mass spectrometry experiments at pH 12.8.[7,8] Note that the k values given in this paper are 1/slope (seconds) obtained from the regression analysis of each run. The agreement is good considering the differences in pH, ionic strength conditions, and type of measurement.

Figure 1 shows a graph of k_{obs} versus $[H^+]$ for TcO_4^-. In the neutral and basic regions, the rate constant becomes very small, and in fact, only in one run where $[OH^-] = 0.10$ M were we able to follow the reaction long enough to see a change significantly larger than the experimental error. This rate constant was essentially the same as those measured in the neutral region. From these results, we conclude that there is no significant $[OH^-]$ term with TcO_4^- and that the rate constant measured at $[OH^-] = 0.10$ M represents the pH independent term. This is different than observed with ReO_4^-, for which the hydroxide dependent term in the rate expression was $k_{OH}[H_2O][ReO_4^-][OH^-]$.[7,8] The data shown in Figure 1 was fitted by a nonlinear least-squares program to the equation $k = a[H^+]^2 + b$. The fit was satisfactory when compared to the estimated experimental error, and thus we concluded that the rate expression for TcO_4^- has the form $k_{obs} = k_H[H^+]^2 + k_O$

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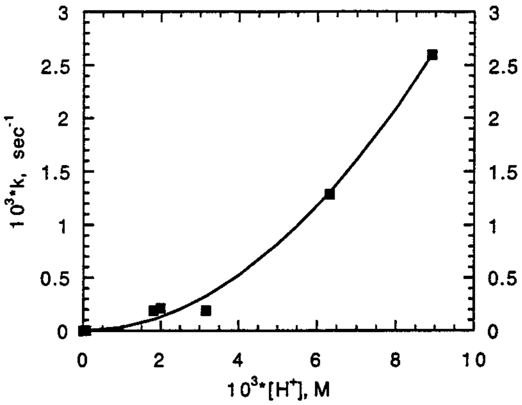

Figure 1. $TcO_4^-{-}H_2O$ exchange rate constants vs $[H^+]$ at 25 °C, showing a second-order dependence on hydrogen ion.

and at 25 °C the values are $k_H = 3.26(15) \times 10^4\ M^{-1}\ s^{-1}$ and $k_O = 1 \times 10^{-8}\ s^{-1}$. From our data it is difficult to give an estimated error for the k_O term.

An experiment was conducted to ascertain the effect(s) of citrate ion (0.10 M) on the oxygen exchange of TcO_4^- and ReO_4^-. The alkaline region was chosen so that any potential general acid catalysis would not be present (citric acid: $pK_a =$ 3.06, 4.74, 5.40). The k_{obs} for ReO_4^- in 0.10 M citrate ion solution was $1.02 \times 10^{-5}\ s^{-1}$ at a pH of 7.0. The rate constant extimated for this pH from the data of Murmann et al.[7−9] in the absence of citrate ion is $(3-5) \times 10^{-7}\ s^{-1}$. Citrate ion caused an appreciable rate enhancement (ca. 25-fold) in the near neutral region. This difference would be expected if ReO_4^- was able to expand its coordination sphere by reversibly coordinating with citrate ion. This coordination number expansion for ReO_4^- was strongly suggested by Vajo et al.[6] in their study of the reduction of ReO_4^- in the presence of oxalate and citrate ions. They showed convincingly that a complex or complexes with Re(VII) were formed and that the formation constants were reasonably small. On the other hand, the rate of oxygen exchange remained low for TcO_4^- in 0.10 M citrate (pH 9.75), of about the same magnitude as when citrate ion was not present. These results indicate that TcO_4^- does not reversibly form a complex with citrate ion which provides a route to oxygen exchange, lending support to the idea that TcO_4^- does not expand its coordination number as ReO_4^- appears to do.

In an effort to establish perrhenate complexes and discern their structure, 1:1 mixtures of $NaReO_4$ and citric acid or sodium oxalate solutions were slowly evaporated. The crystals which formed were only those of the starting materials. Thus, no confirmation of complex formation was obtained but neither is it established that they do not exist; it is established only that they do not crystallize preferentially.

The mechanism of oxygen exchange for the k_O and $k_H{}^2$ paths is predominately dissociative, and for the k_{OH} pathway associative behavior is strongly suggested.[7,8] There is no evidence suggesting that the pertechnetate ion associates with OH^- or citrate ion, as does perrhenate. The associative process for perrhenate appears to involve coordination number expansion. In order for citrate ion to assist in oxygen exchange through coordination, the bonding to the perrhenate oxygens must be weakened and reversible dissociation facilitated. Exchange might also occur by coordination of citrate ion and solvent water. The rate-controlling step then would involve perrhenate oxygens exchanging with coordinated waters by proton transfer. At this time evidence for these details is not available.

Conclusion

The observed rate of solvent oxygen exchange on TcO_4^- shows a two-term rate law similar to that observed in the acidic and neutral region with ReO_4^-. There is no $[OH^-]$ dependent term, as found with ReO_4^-. In the presence of citrate ion, the rate increases with ReO_4^- but not with TcO_4^- in the neutral pH region. Both of these observations suggest coordination number expansion for ReO_4^- but not for TcO_4^-, consistent with previous observations on the differences in behavior between TcO_4^- and ReO_4^- when they would not have been expected on structure alone.

Acknowledgment. The authors gratefully acknowledge Mallinckrodt Medical, Inc., of St. Louis, MO, for partial financial support of this work and the National Science Foundation (NSF CHE 9221835) for the NMR facility. The authors would like to thank Dr. Wei Wycoff for her assistance in collecting the NMR data.

Supporting Information Available: Table of $TcO_4^-{-}H_2O$ exchange rate constants and plot of $\ln(1 - F)$ as a function of time. This material is available free of charge via the Internet at http://pubs.acs.org.

IC9902830