pH range 4–6.8 contain low-spin heme *c* groups that are axially ligated by an imidazole nitrogen atom of His-18 and the sulfur atom of Met-80.[8] Although the native protein conformation isolates the heme *c* group from solvent molecules, it is probable that reagents with hydrophobic, π-conjugated ligands can penetrate the hydrophobic region surrounding the protein redox center, thereby facilitating electron transfer. More specifically, in recent work we have estimated[1] that the edge of the coordinated pyridine comes within 4 Å of the heme *c* edge at the instant of electron transfer from the protein redox center to $[Ru(NH_3)_5py]^{3+}$.

Addition of one proton to ferrocytochrome *c* with $K = 1.40 \times 10^3$ M^{-1} produces a species that is able to transfer an electron to $[Ru(NH_3)_5py]^{3+}$ more rapidly. Neither the spin state nor the axial ligation of this species, H^+-ferrocytochrome *c*, is known for certain. A few studies have been published that bear on this point, but they are not definitive. It is known, for example, that CO binds slowly to ferrocytochrome *c* just below pH 3, but no binding is observed between pH 3 and 4.[13] Changes in ^1H NMR spectra are observed[14] between pD 4.5 and 3 upon addition of DCl to D_2O solutions of ferrocytochrome *c*; these changes are substantial between pD 4.5 and 3, and possible explanations include the presence of a high-spin heme *c* or axial ligand loss (or both). The evidence for a spin-state change in this pH range is not compelling, however, and the CO binding experiments[13] are more easily reconciled by assuming that the heme *c* group is still axially ligated and low spin. The latter assumption also is supported by the observation that the electronic absorption spectrum of ferrocytochrome *c* does not vary significantly in the pH range 1–6.[7]

Whatever the structural change may be, it is clear that the protonated protein is oxidized by a variety of reagents more rapidly than is ferrocytochrome *c*.[6-8] The higher reactivity must be related to some type of structural perturbation because the analogous protonated form of the oxidized protein, H^+-ferricytochrome *c*, is reduced by $[Ru(NH_3)_6]^{2+}$ more rapidly than is native ferricytochrome *c*.[15] Based on the value of *K* for ferrocytochrome *c*, it is reasonable to suggest that the site of protonation is the imidazole ring of His-26. This site is protonated below pH 3.5 in ferricytochrome *c*,[16] and it would be expected[17] to exhibit similar behavior in the reduced protein. A small conformational change induced in the heme *c* region by protonation of His-26 could easily account for the increased outer-sphere electron-transfer reactivity of H^+-ferrocytochrome *c*, with the assumption that reagent access to the protein redox center was somewhat greater in the perturbed structure. Other factors being equal, it would require only a small change in the percentage of the heme *c* surface available for reagent contact to account for the observed increase in the rate constant for oxidation of the protonated form of the protein by $[Ru(NH_3)_5py]^{3+}$ ($k_4/k_3 \approx 6$).

Our scheme for the oxidation of ferrocytochrome *c* by $[Ru(NH_3)_5py]^{3+}$ below pH 4 is simpler than the one proposed[7] by Brunschwig and Sutin for the oxidation of the protein by $[Co(phen)_3]^{3+}$ at low pH. In the latter case, a maximum in the pH/rate profile was found at pH 2.9, and our results do not indicate any such maximum. Therefore, we need only postulate two different reactive protein species rather than the three that are required by the kinetic data collected by Brunschwig and Sutin. It is likely that the difference in kinetic behavior is due to the presence of chloride in the ferrocytochrome *c*/$[Co(phen)_3]^{3+}$ solutions, one reasonable possibility being that binding of Cl^- to the protein produces at least one additional species at low pH. Clearly, more work will be required to determine whether chloride-binding effects are sufficient to account for the difference in pH/rate profiles for the $[Co(phen)_3]^{3+}$ and $[Ru(NH_3)_5py]^{3+}$ oxidations of ferrocytochrome *c*.

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Registry No. Ferrocytochrome *c*, 9007-43-6; $[Ru(NH_3)_5py]^{3+}$, 33291-25-7.

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(14) McDonald, C. C.; Phillips, W. D. *Biochemistry* **1973**, *12*, 3170.
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(17) Drew, H. R.; Dickerson, R. E. *J. Biol. Chem.* **1978**, *253*, 8420.

Contribution from the Department of Chemistry,
Indiana University, Bloomington, Indiana 47405

Kinetic Study of Oxygen Exchange in $[Re(CO)_6][PF_6]$ with $H_2{}^{17}O$

ROBIN L. KUMP and LEE J. TODD*

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The exchange between ^{17}O-enriched water and $[Re(CO)_6][PF_6]$ in CH_3CN has been investigated with utilization of ^{17}O NMR spectroscopy. Oxygen-17 NMR spectroscopy offers several advantages over other techniques for following oxygen-exchange reactions. The rate of exchange follows the equation $R_O = k_{ex}[Re(CO)_6]^+][H_2O]^2$. The second-order dependence of H_2O for the reaction indicates the important role of H_2O in the exchange of oxygen atoms on the carbonyl ligand and H_2O. The reaction rate has activation parameters of $\Delta H^{\ddagger} = 11.5 \pm 0.7$ kcal/mol and $\Delta S^{\ddagger} = -33.6 \pm 1.8$ cal/(deg mol). The reaction mechanism for oxygen exchange is discussed.

Introduction

Recently, we have shown useful applications of oxygen-17 NMR in the structural characterization of transition metal carbonyl compounds.[1,2] In the present paper we will demonstrate the potential of oxygen-17 NMR as an aid to deducing mechanistic pathways of oxygen enrichment. The establishment of a mechanism of enrichment for metal carbonyl compounds should lead to new methods for enriching a large range of carbonyl complexes and provide further basic information about oxygen-exchange processes.

Muetterties[3] has observed that $Re(CO)_6{}^+$ readily exchanges the carbonyl oxygens with the oxygen atoms of $H_2{}^{18}O$. The exchange was believed to occur by nucleophilic attack at a

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(1) Kump, R. L.; Todd, L. J. *J. Chem. Soc., Chem. Commun.* **1980**, 292.
(2) Kump, R. L.; Todd, L. J. *J. Organomet. Chem.* **1980**, *194*, C43.
(3) Muetterties, E. L. *Inorg. Chem.* **1965**, *4*, 1841.

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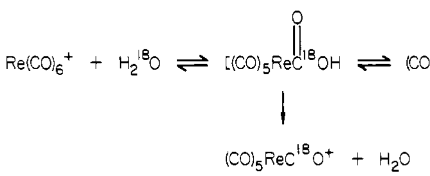
carbon atom by OH^- or OH_2 to give $(CO)_5ReCOOH$ or $(CO)_5ReC(OH)_2^+$. Darensbourg[4] has studied this reaction with oxygen-18 water in CH_3CN by monitoring the infrared stretching frequencies of the carbonyl ligands. Mixing and overlap of the stretching modes permitted only qualitative information of the reaction pathway to be obtained, however. Darensbourg proposed that a $(CO)_5ReCOOH$ intermediate is in equilibrium with the starting cationic carbonyl derivative. Rapid exchange of a proton between the two oxygens and subsequent loss of the OH^- group completes the enrichment process. The cycle is repeated as enrichment continues.



Our goal was to determine the exact role of H_2O in the exchange process: was the attacking nucleophile actually H_2O or OH^-? In addition, we wished to demonstrate from a practical standpoint the advantages ^{17}O NMR spectroscopy has over present techniques for studying oxygen-exchange reactions. We have completed a quantitative kinetic study of the oxygen-exchange reaction between $Re(CO)_6^+$ and H_2O. Our findings are consistent with the previously suggested mechanism involving a M(COOH) intermediate, as well as with a newly proposed mechanism incorporating a water dimer intermediate.

Experimental Section

Reactants and Reagents. $[Re(CO)_6]BF_4$ was prepared by a literature method.[4] The freshly prepared tetrafluoroborate salt was washed with anhydrous ether and air-dried. The salt was dissolved in H_2O and then filtered. The filtrate was added to a solution containing excess $[NH_4]PF_6$ to precipitate $[Re(CO)_6]PF_6$. The white precipitate was washed with water and vacuum-dried. So that small amounts of trapped impurities could be removed, the hexafluorophosphate salt was dissolved in dry CH_3CN and filtered and the filtrate evaporated to dryness.

Tetrabutylammonium hydroxide (40%) was obtained from Aldrich Chemical Co., and $HClO_4$ (70%) was obtained from Mallinckrodt Chemical Co. Both were titrated against standard acid and base solutions to determine their molarity. $HClO_4$ does not exchange oxygen atoms with H_2O in acetonitrile solutions.[5] Enriched water (45.2% ^{17}O) was purchased from Yeda Research and Development Co., Rehovot, Israel, and diluted to 4.5% ^{17}O enrichment for all experiments with water distilled from $KMnO_4$. Reagent grade acetonitrile was purified by distillation from CaH_2 under nitrogen. $Re_2(CO)_{10}$ was purchased from Strem Chemical Co., Newburyport, Maine, and used without further purification.

Kinetics Procedure. In a typical experiment, unenriched $[Re(CO)_6]PF_6$ (0.034 g) was dissolved in 2 mL of CH_3CN in an NMR tube and 12.6 μL[6] of $H_2{}^{17}O$ was injected into the tube. A vortex suppressor was used and the sample was spun at 22 Hz in the spectrometer. The intensity of the H_2O signal was monitored to follow the reaction.

A Varian XL-100-15 spectrometer operating in the pulsed Fourier transform mode at 13.57 MHz was used. The fast relaxation of the oxygen nuclei allowed a 90° pulse followed by a pulse interval of 0.11 s to be used for each transient. A Nicolet T_1 software program was utilized to automate the data sampling. Each sample file contained 2K data points, and 1024 transients were collected to obtain an adequate signal-to-noise ratio. The unavoidable time required for data collection meant the data for the first ~10% of the reaction was not as accurate as the latter data (i.e., as time passed, the sampling time became small compared to the rate of the reaction). The data for the first ~10% of the reaction in the fast exchanges were therefore not used to calculate the rates.

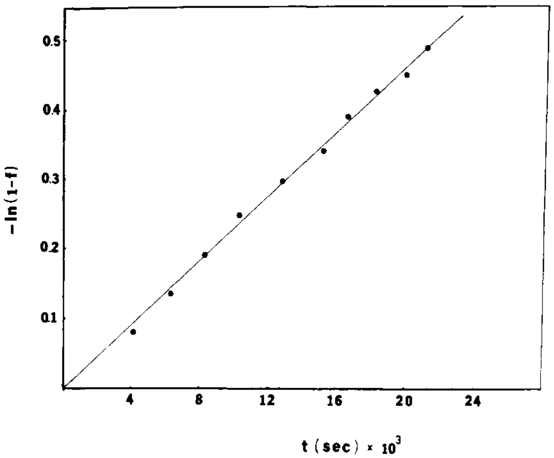


Figure 1. Typical exchange plot where $[Re(CO)_6^+] = 0.068$ M and $[H_2O] = 0.334$ M.

The kinetic data were treated according to the first-order McKay expression[7]

$$-\mathrm{d}\ln(1-F)/\mathrm{d}t = ((a+b)/ab)R_O$$

where $(1-F)$ is defined as the fraction of the reaction that has occurred and a and b are the atoms exchanging and are expressed in molar concentrations. In the reaction under consideration, $a = 6 \times [Re(CO)_6^+]$ and $b = [H_2O]$. R_O is defined as the rate of exchange with respect to oxygen atoms. This equation has been successfully used with other oxygen complexes that exchange with labeled $H_2{}^*O$.[8-10]

Graphs of $-\ln(1-F)$ or $-\ln((I_t - I_\infty)/(I_0 - I_\infty))$ vs. time were plotted and were linear for the 3 to 4 half-lives which were measured. The terms I_0, I_t, and I_∞ are defined as the signal intensities at time $t = 0$, t = time reaction was sampled, and $t = \infty$ (at exchange equilibrium). I_0 was independently obtained by using a blank sample of $H_2{}^{17}O$ (4.5% ^{17}O) in 2 mL of CH_3CN. A least-squares analysis was used to obtain the numerical values of the slopes which were then multiplied by the quantity $ab/(a+b)$ to calculate R_O. The reproducibility of the ^{17}O NMR measurements was found not to vary by more than 5% from one run to another. The precision in the obtained values proved to be nearly as good (4–8% error).

Isotopic effects were neglected[11,12] in the above rate determinations since the quantity of the ^{17}O isotope in H_2O for the experiments was very small (4.5%).

Results and Discussion

Previous kinetic studies of isotopic oxygen exchange have primarily utilized infrared and mass spectroscopy. Both of these techniques have severe experimental disadvantages in kinetic studies. An aliquot of the reaction solution must be periodically removed and immediately analyzed when infrared spectroscopy is used or the entire reaction must be quenched for mass spectroscopic analysis. Since neither H_2O nor the complex is usually analyzed directly by mass spectroscopy, the oxygen present must be converted to a gas, most often CO or CO_2.[5] This step requires the use of elaborate reaction vessels and the time-consuming isolation and preparation of a sample for each data point collected. Infrared spectroscopy suffers from the disadvantage of overlapping CO absorption bands when more than one carbonyl ligand is present. Direct measurements by ^{17}O NMR spectroscopy avoids all these problems.

The linear graph shown in Figure 1 and those obtained at other concentrations for both H_2O and $Re(CO)_6^+$ demonstrate

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(5) Samuel, D.; Silver, B. L. *Adv. Phys.-Org. Chem.* **1965**, *3*, 123.

(6) The cost of $H_2{}^{17}O$ for these types of experiments at the designated concentrations and quantities is minimal: 12.6 μL of $H_2{}^{17}O$ (4.5% ^{17}O) costs ~\$0.25, calculated from a market price of \$150 for 1 g of $H_2{}^{17}O$ (≈50% ^{17}O).

(7) McKay, H. A. C. *Nature (London)* **1938**, *142*, 997.

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Table I. Exchange Rates[a] in CH_3CN at 32 °C

$[Re(CO)_6^+]$, M	$[H_2O]$, M	$10^6 R_O$, M s^{-1}
0.034	0.680	9.61 ± 0.69
0.034	0.680	9.35 ± 0.72
0.068	0.340	4.50 ± 0.20
0.068	0.340	4.70 ± 0.21
0.034	0.340	2.31 ± 0.09
0.034	0.340	2.29 ± 0.12
0.068	0.170	1.14 ± 0.06

[a] $\bar{k}_{ex} = (5.84 \pm 0.90) \times 10^{-4}$.

Table II. Exchange Rates with Added OH^- and H^+ ($[Re(CO)_6^+]$ = 0.034; $[H_2O]$ = 0.340)

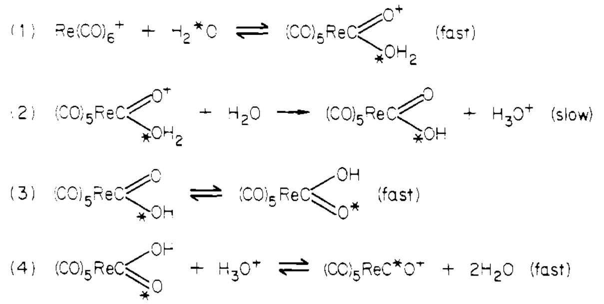
$10^6 R_O$, M s^{-1}	$[OH^-]$, M	$[H^+]$, M	$[NEt_3]$, M
2.30 ± 0.13			
7.7 ± 2.1	0.0015		
5.7 ± 1.4	0.00015		
1.80 ± 0.07		0.00015	
6.3 ± 1.7			0.0018

Table III. Temperature Dependence of Exchange Rates[a] ($[Re(CO)_6^+]$ = 0.034; $[H_2O]$ = 0.340)

$10^6 R_O$, M s^{-1}	temp, °C	$10^6 R_O$, M s^{-1}	temp, °C
2.30 ± 0.13	32	13.0 ± 0.7	60
6.60 ± 0.33	50	12.7 ± 0.7	60

[a] E_a = 12.1 ± 0.8 kcal/mol. $\Delta S^‡ = -33.6 \pm 1.8$ cal/(deg mol), $\Delta H^‡$ = 11.5 ± 0.7 kcal/mol.

Scheme I



that the six carbonyl oxygens are exchanging with H_2O at equal rates. This would be expected since the carbonyls are all chemically equivalent.

Table I gives the reaction rates at the respective concentrations. The ionic strength was not kept constant by the addition of another salt when the $Re(CO)_6^+$ concentration was varied because of the possible difference in the solvation of H_2O toward the salts. The experimental results, however, do not seem to be adversely affected by the change in ionic strength. The overall order of the reaction is third order: first order in the metal complex and *second* order in H_2O. The rate expression for the oxygen exchange is thus

$$\text{rate} = k_{ex}[Re(CO)_6^+][H_2O]^2$$

Table II shows the rate dependence upon OH^- and H^+ concentration. The amount of $[OH^-]$ present in a dilute solution of H_2O in CH_3CN solvent is $\sim 5 \times 10^{-10}$ M.[13] Estimating the amount of $[OH^-]$ (for CH_3CN[14] in H_2O) solely from log K_a = 10 suggests a very small and similar concentration reflecting the weakly basic property of CH_3CN. Therefore, the concentrations added are in large excess of those initially present in solution. The addition of $[OH^-]$ increases the rate of oxygen exchange. Larger errors in the oxygen-exchange rates were also obtained when $[OH^-]$ was increased because of the minor secondary reaction which occurs with $[OH^-]$ addition. Thus an increase in $[OH^-]$ increases the rate of formation of $HRe(CO)_5$ presumably from a carboxylic intermediate.

$$(CO)_5ReC(O)OH + OH^- \rightarrow (CO)_5ReCO_2^- + H_2O \rightarrow (CO)_5ReH + CO_2 + OH^-$$

Darensbourg[15] has also noted this same secondary reaction for the oxygen-exchange reaction involving $H_2{}^{18}O$ and $Mn(CO)_4(diphos)^+$. However, in both cases, the reaction path leading to metal hydride formation is not noted for the reaction of $Mn(CO)_4(diphos)^+$ or $Re(CO)_6^+$ with only H_2O even over long reaction periods. The values in Table II were determined from data up to only the first half-life. (With the passage of time, less $Re(CO)_6^+$ is present to exchange and the rate of reaction slows down.) It should be stressed that the oxygen-exchange reaction is still the dominant reaction taking place during the measurements (as indicated by infrared spectra) at the base concentrations listed in Table II. Therefore, the values for rates of oxygen exchange with increases in $[OH^-]$ and $[H_3O^+]$ can be applied to interpretations of the oxygen exchange mechanism.

Table III displays both the temperature effect on the rate of oxygen exchange and the calculated activation parameters. The parameters are similar to values found for organic ketones which undergo oxygen exchange.[5]

When 90% D_2O (4.5% ^{17}O) was added instead of H_2O, the rate of exchange slowed by a factor of 3.3 (k_{H_2O}/k_{D_2O} = 3.3).

The experimental results clearly indicate that H_2O and not OH^- is the important species in the oxygen-exchange mechanism under neutral pH conditions. (At high pH, another mechanism is probably involved.) The results also reveal the dependence upon *two* water molecules in the exchange process, a fact which was not known or alluded to in any previous work. The first-order isotope effect (k_{H_2O}/k_{D_2O} = 3.3) observed when D_2O is substituted for H_2O demonstrates that oxygen–hydrogen bond breaking or formation to be the rate-determining step. A mechanism which explains the rate expression

$$R_O = k_{ex}[Re(CO)_6^+][H_2O]^2$$

is illustrated in Scheme I.

Step 2 which involves the hydrogen abstraction of a proton by a second water molecule is consistent with both the experimental results and the fact that acetonitrile is a weaker base than H_2O.[13,14] The rate-determining step is therefore step 2 based upon the results from the D_2O experiment. Step 3 can be ruled out as the rate-determining step because proton transfer is usually a very fast process (10^{10} s^{-1}),[16,17] especially between two oxygen atoms. Therefore, the proton transfer in step 3 is presumed to be rapid in conjunction with experimental data. The large $t_{1/2}$ values for the different runs ranging from ~120 to 1220 min suggest that a proton transfer would not be rate determining.

This mechanism explains also the increase of the rate with added $[OH^-]$ since more of the metal carboxylic acid would be formed. Though $[OH^-]$ does not appear explicitly in the rate expression, the mechanism of Scheme I should show a general base dependence and indeed does. The lack of any dramatic increase (10–100 times) of the rate with a very large

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(13) Holmes, J. R.; Kivelson, D.; Drinkard, W. C. *J. Am. Chem. Soc.* **1962**, 4677.

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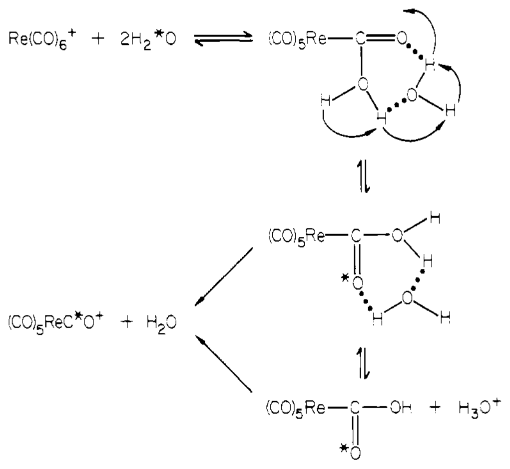
(16) Bell, R. B. "The Proton in Chemistry", 2nd ed.; Cornell University Press: Ithaca, NY, 1973.

(17) Barnett, R. E. *Acc. Chem. Res.* **1973**, *6*, 41.

Scheme II



increase of [OH^-], however, argues against the dominant mechanism being one in which OH^- is the attacking nucleophile.

$$Re(CO)_6^+ + OH^- \rightarrow (CO)_5ReC(O)OH$$

With regard to our proposed mechanism, the lack of a dramatic rate enhancement with increased OH^- concentration can be explained either in terms of OH^- competition for the carbon site with the more abundant (300–3000 times) H_2O, or a concerted mechanism is operating. In addition, the H_2O solvation sphere about $Re(CO)_6^+$ may limit the access of the better nucleophile, OH^-, to the carbon site, thus mitigating the effects of increasing base concentration.

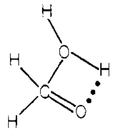
The mechanism also can be used to explain the oxygen-exchange rate decrease upon the addition of acid. The equilibrium in step 2 would be shifted to the left, decreasing the amount of metal carboxylic acid present.

A mechanism which involves the simple nucleophilic attack of OH^- at the carbonyl carbon may indeed occur at high pH values, but it can be ruled out as the dominant mechanism when no excess of [OH^-] is present. The existence of an equilibrium between two water molecules which would form OH^- might explain the second-order dependence on H_2O, but the concentration of OH^- produced in this manner would be negligible, and, as mentioned previously, the concentration of OH^- formed from the solvent and H_2O ($CH_3CN + H_2O \rightleftharpoons CH_3CNH^+ + OH^-$) is also very small.

Of course, second-order dependence on H_2O does not require the operation of a step-wise mechanism, and a concerted mechanism involving a pathway such as that outlined in Scheme II might in fact be occurring. Exchange could occur at several different points in such a mechanism. Simple proton exchange among the oxygens and then loss of the two water molecules would lead to enrichment, or the cyclic intermediate could also produce both a transient MC(O)OH species and H_3O^+ which could then undergo exchange as indicated in Scheme I. The isolation of stable metal carboxylic acid derivatives such as $(C_5H_5)Re(CO)(NO)(CO_2H)$,[18] $C_5H_5FeL_2(CO_2H)$[19] (where L = CO, PPh_3), and $IrCl_2(CO_2H)(CO)L_2$[20] (where L = Me_2PhP, Me_2PhAs) substantiate the possible intermediacy of metal derivatives containing the COOH ligand in our exchange mechanism. In fact, the $Re(CO)_6^+$ complex is itself prepared[21] from the ester, $(CO)_5ReC(O)OR$.

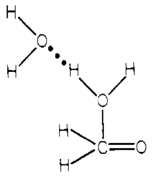
$$(CO)_5ReC(O)OR + HCl \rightarrow [(CO)_5Re(CO)][Cl] + HOR$$

Recently, Schowen and Maggiora[22] have postulated the involvement of a second water molecule in the hydration of formaldehyde. The transition state for the adduct involving only one water molecule is energetically unfavorable.



Their theoretical calculations indicate that a reduction in the energy required for hydration occurs when a second water molecule participates in the transition state.

Our experimental findings also support the importance of two water molecules in the oxygen-exchange process, and we propose that the exchange mechanism involves intermediates very similar to either I or II.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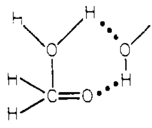
II

Conclusions

Even though oxygen-17 NMR spectroscopy can be used as a powerful tool in kinetic studies, as we have shown above, to date the elucidation of enrichment pathways with the use of ^{17}O NMR spectroscopy has been relatively unexplored.[23-26] With the renewed interest in the water gas shift reaction

$$CO + H_2O \rightleftharpoons H_2 + CO_2$$

there have been recent discoveries utilizing metal carbonyl compounds[27-29] as catalysts. It is probable that a better understanding of the mechanism of these catalysts will be forthcoming with studies using $H_2{}^{17}O$ and ^{17}O NMR spectroscopy.

Acknowledgment. This work was supported by the National Science Foundation through Grant CHE 78-08719.

Registry No. [$Re(CO)_6$]PF_6, 38656-75-6; H_2O, 7732-18-5; ^{17}O, 13968-48-4.

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