Organometallics **2005,** *24,* 2780−2788

Proton−Deuteron Exchange Reactions of Methyltrioxorhenium(VII) in Organic Solvents

Mitsuru Matsumoto and James H. Espenson*

Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa 50011

Received December 8, 2004

Rate constants for the proton/deuteron (H/D) exchange of methyltrioxorhenium(VII) (MTO) were determined in four organic solvents by means of time course ^{1}H NMR measurements. Exchange between MTO and a deuterium donor proceeds only in the presence of a Lewis base; the reaction does not take place in neutral or acidified solutions. The kinetics depends on the bases, deuterium donors, and solvents. The observed pseudo-first-order rate constants (k_ψ) are negligibly small when coordinating bases are used but increase with noncoordinating bases. A direct relationship was found between k_ψ and the pK_a values of the conjugate acids of the bases. With phenol-d_6 as a deuterium donor (D) and 2,6-lutidine as a base (B), the rate law varies with solvents: $k_\psi = k_a[D][B]$ in benzene-d_6 ($k_a = 1.95 \times 10^{-3}$ kg^2 mol^{-2} s^{-1}); $k_\psi = k_a\kappa[D][B]/(1 + \kappa[D])$ in chloroform-d ($k_a = 1.41 \times 10^{-2}$ kg mol^{-1} s^{-1}, $\kappa = 0.79$ kg mol^{-1}); $k_\psi = k_a[B]$ in acetone-d_6 and acetonitrile-d_3 ($k_a = 1.22 \times 10^{-2}$ and 3.87×10^{-2} kg mol^{-1} s^{-1}, respectively) at 24.8 °C. The same treatment applies to the methanol-d_4/lutidine system in benzene-d_6, once allowance is made for formation of an MTO−methanol adduct. Reasonably rapid exchange under mild conditions reflects the acidic character of MTO, which may arise from its base-promoted keto/enol tautomerization. Three consecutive steps are suggested for the reaction mechanism: attack of a base on an MTO methyl proton, isomerization to the enol intermediate ($\mathbf{I_2}$), and H/D exchange between $\mathbf{I_2}$ and a deuterium donor.

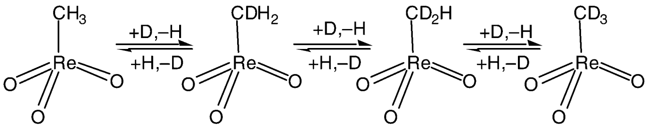
Introduction

Methyltrioxorhenium(VII), CH_3ReO_3 or MTO, catalyzes reactions of hydrogen peroxide, the mechanisms of which have been extensively studied.[1−5] Whereas no H/D exchange of the CH_3 group was found in deuterioxide media,[1] partially deuterated MTO (CDH_2ReO_3, MTO-d: Scheme 1) was detected by ^{1}H NMR spectroscopy in nitromethane-d_3 solution in the presence of pyridine at 296 K.[6] The mechanism was not resolved, but the observation of exchange under mild conditions could imply the indirect involvement of the enol form of MTO, $CH_2{=}Re(O)_2OH$. In Scheme 1 the reaction steps are not intended to describe unimolecular reactions but involve concentrations of heterocyclic bases and deuterium donors, as will be described.

The energy difference between the keto and enol forms of MTO has been estimated to be 89 kJ mol^{-1} by a density functional theory calculation.[7] Clearly, the enol form of MTO by itself is out of range as an accessible intermediate, with pK_{ke} ca. 15−16. The estimate of pK_{ke} was made by approximating $\Delta G° \approx \Delta H°$, because $\Delta S°$ can be taken as ~0 for a reaction with nearly identical species on each side of the chemical equation. In the solid state the enol form of MTO was generated by UV irradiation and identified by its IR spectrum at 14 K in a solid argon matrix.[7,8] In solution, although the enol form of MTO has not been detected, it was reasonably proposed as the active intermediate in olefin metathesis.[9] We have suggested the involvement of enol MTO as the reactive intermediate in the synthesis of a complex in which the resulting Re−CH_2−pyridine unit was interpreted as the consequence of nucleophilic attack of pyridine at the methylene group of the enol.[10]

The carbonyl group of a ketone increases the acidity of the α-proton, because the enol tautomer is stabilized

Scheme 1. H/D Exchange Reactions of MTO



---

* To whom correspondence should be addressed. E-mail: espenson@iastate.edu.

[1] Espenson, J. H.; Abu-Omar, M. M. *Adv. Chem. Ser.* **1997**, *No. 253*, 99−134.

[2] Li, M.; Espenson, J. H. *J. Mol. Catal. A* **2004**, *208*, 123−128.

[3] Bouh, A. O.; Espenson, J. H. *J. Mol. Catal. A* **2003**, *200*, 43−47.

[4] Gisdakis, P.; Antonczak, S.; Kostlmeier, S.; Herrmann, W. A.; Rosch, N. *Angew. Chem., Int. Ed.* **1998**, *37*, 2211−2214.

[5] Vassell, K. A.; Espenson, J. H. *Inorg. Chem.* **1994**, *33*, 5491−5498.

[6] Wang, W.-D.; Espenson, J. H. *J. Am. Chem. Soc.* **1998**, *120*, 11335−11341.

[7] Morris, L. J.; Downs, A. J.; Greene, T. M.; McGrady, G. S.; Herrmann, W. A.; Sirsch, P.; Scherer, W.; Gropen, O. *Organometallics* **2001**, *20*, 2344−2352.

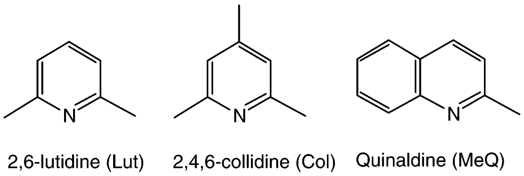
[8] Morris, L. J.; Downs, A. J.; Greene, T. M.; McGrady, G. S.; Herrmann, W. A.; Sirsch, P.; Gropen, O.; Scherer, W. *Chem. Commun.* **2000**, 67−68.

[9] Hoffman, D. M. *Comprehensive Organometallic Chemistry II*; Casey, C. P., Ed.; Pergamon: Oxford, U.K., 1995; Vol. 6, pp 231−255.

[10] Zhang, C.; Guzei, I. A.; Espenson, J. H. *Organometallics* **2000**, *19*, 5257−5259.

10.1021/om049029s CCC: $30.25

Chart 1. Structures of the N-Heterocyclic Bases



by conjugation.[11] The keto/enol equilibrium constants of carbonyl compounds are generally small, pK_{ke} 6−9; therefore, the presence of acid or base is needed to observe H/D exchange.[11] Even though MTO is acidic, pK_a ca. 7.5 at 25 °C,[12−14] bases cause the rapid and irreversible decomposition of MTO to perrhenate ions and methane.[15] We have yet to realize exchange in acidic aqueous solution.[16,17]

For metal-bonded alkyl groups, various H/D exchange reactions have been reported;[18] however, the role of metal−carbon double-bond formation is varied. Slow deuterium incorporation to a metal-bonded alkyl group has been observed for Mo[19] and W[20−22] complexes, where the reaction proceeds via the formation of a metal−carbon double bond and requires high temperature and extended times. In turn, fast H/D exchange reactions are found in alkyl complexes of Os,[23] Ta,[24] and Pt,[25−27] where the participation of metal−carbon double bonds is insignificant. As for rhenium complexes, very slow H/D exchange was observed in the methylene proton of $Re_2(\mu\text{-}CH_2)(\mu\text{-}O)O_2Me_4$ and the reaction is decelerated by the addition of acid.[28]

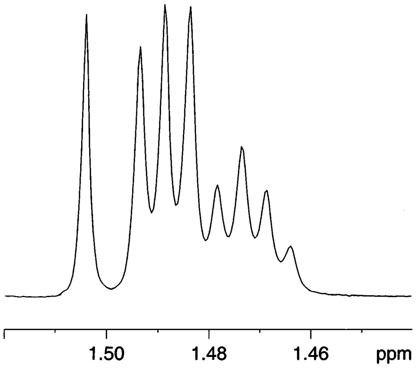


Figure 1. ^{1}H NMR spectra of MTO-d_n (n = 0−2) after 7 h at 323 K. Concentrations: 0.05 mol kg^{-1} of MTO, 1.0 mol kg^{-1} of CD_3OD, 0.6 mol kg^{-1} of pyridine-d_5.

This article reports studies of the H/D exchange of MTO catalyzed by weakly coordinating N-heterocyclic bases (Chart 1). In the presence of an excess amount of deuterium donor, exchange proceeds to completion in three sequential steps. The kinetics depends on the solvents, bases, and deuterium donors used. Nonetheless, a general mechanism can be assigned; the near absence of exchange when one uses a Lewis base that coordinates extensively to the rhenium center will also be discussed.

Experimental Section

MTO was synthesized by a literature method.[29] Other chemicals were purchased from commercial sources and used without further purification. Throughout this study, we used molality as the concentration unit to enable facile sample preparation and to avoid wasting deuterated reagents. A Bruker DRX-400 MHz spectrometer was used to record ^{1}H NMR spectra at 298.0(1) K. The ^{1}H chemical shifts of MTO were measured relative to the residual ^{1}H resonances of the deuterated solvents.

Rate constants were calculated from ^{1}H NMR time course experiments; the signal intensities were used instead of peak areas, because the resonances of MTO and MTO-d_n species overlap; see Figure 1. The intensities of the singlet of MTO, the center peak of the MTO-d triplet, and the center peak of the MTO-d_2 quintet were used for the determinations. For reactions with half-lives greater than 30 min, averaged spectra from 16 scans were used; for faster reactions, only a single-scan spectrum was used.

The rate constants for the three steps of H/D exchange were calculated from eqs 1−3,[30] in which A, B, and C correspond to the peak intensities of MTO-d_n, n = 0, 1, 2. The observed rate

$$A = A_0 \exp(-k_\psi^{01}t) \tag{1}$$

$$B = \frac{k_\psi^{01}A_0}{k_\psi^{12} - k_\psi^{01}}\{\exp(-k_\psi^{01}t) - \exp(-k_\psi^{12}t)\} \tag{2}$$

$$C = \frac{k_\psi^{01}k_\psi^{12}A_0}{(k_\psi^{12} - k_\psi^{01})(k_\psi^{23} - k_\psi^{01})}\exp(-k_\psi^{01}t) + \frac{k_\psi^{01}k_\psi^{12}A_0}{(k_\psi^{01} - k_\psi^{12})(k_\psi^{23} - k_\psi^{12})}\exp(-k_\psi^{12}t) + \frac{k_\psi^{01}k_\psi^{12}A_0}{(k_\psi^{01} - k_\psi^{23})(k_\psi^{12} - k_\psi^{23})}\exp(-k_\psi^{23}t) \tag{3}$$

constant for the loss of MTO, k_ψ^{01}, was calculated directly from the decrease of MTO signal intensity. The second-step rate constant, k_ψ^{12}, was calculated from the rise and fall of the MTO-d signal intensity with k_ψ^{01} fixed at its established value. Likewise, the third-step rate constant k_ψ^{23} was calculated from

---

[11] Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry,* 3rd ed.; HarperCollins: New York, 1987.

[12] Herrmann, W. A.; Fischer, R. W.; Scherer, W. *Adv. Mater.* **1992**, *4*, 653−658.

[13] Espenson, J. H.; Tan, H.; Mollah, S.; Houk, R. S.; Eager, M. D. *Inorg. Chem.* **1998**, *37*, 4621−4624.

[14] Herrmann, W. A.; Fischer, R. W. *J. Am. Chem. Soc.* **1995**, *117*, 3223−3230.

[15] Herrmann, W. A.; Fischer, R. W.; Rauch, M. U.; Scherer, W. *J. Mol. Catal.* **1994**, *86*, 243−266.

[16] Abu-Omar, M. M.; Hansen, P. J.; Espenson, J. H. *J. Am. Chem. Soc.* **1996**, *118*, 4966−4974.

[17] Brittingham, K. A.; Espenson, J. H. *Inorg. Chem.* **1999**, *38*, 744−750.

[18] Labinger, J. A.; Bercaw, J. E. *Nature* **2002**, *417*, 507−514.

[19] Wada, K.; Pamplin, C. B.; Legzdins, P.; Patrick, B. O.; Tsyba, I.; Bau, R. *J. Am. Chem. Soc.* **2003**, *125*, 7035−7048.

[20] Adams, C. S.; Legzdins, P.; McNeil, W. S. *Organometallics* **2001**, *20*, 4939−4955.

[21] Adams, C. S.; Legzdins, P.; Tran, E. *J. Am. Chem. Soc.* **2001**, *123*, 612−624.

[22] Tran, E.; Legzdins, P. *J. Am. Chem. Soc.* **1997**, *119*, 5071−5072.

[23] Hamilton, D. H.; Shapley, J. R. *Organometallics* **2000**, *19*, 761−769.

[24] Fryzuk, M. D.; Johnson, S. A.; Rettig, S. J. *J. Am. Chem. Soc.* **2001**, *123*, 1602−1612.

[25] Prokopchuk, E. M.; Puddephatt, R. J. *Organometallics* **2003**, *22*, 787−796.

[26] Reinartz, S.; White, P. S.; Brookhart, M.; Templeton, J. L. *Organometallics* **2000**, *19*, 3854−3866.

[27] Shilov, A. E.; Shteinman, A. A. *Coord. Chem. Rev.* **1977**, *24*, 97−143.

[28] Hoffman, D. M.; Wierda, D. A. *J. Am. Chem. Soc.* **1990**, *112*, 7056−7057.

[29] Herrmann, W. A.; Kratzer, R. M.; Fischer, R. W. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2652−2654.

[30] Capellos, C.; Bielski, B. H. J. *Kinetic Systems: Mathematical Description of Chemical Kinetics in Solution*; Wiley-Interscience: New York, 1972.

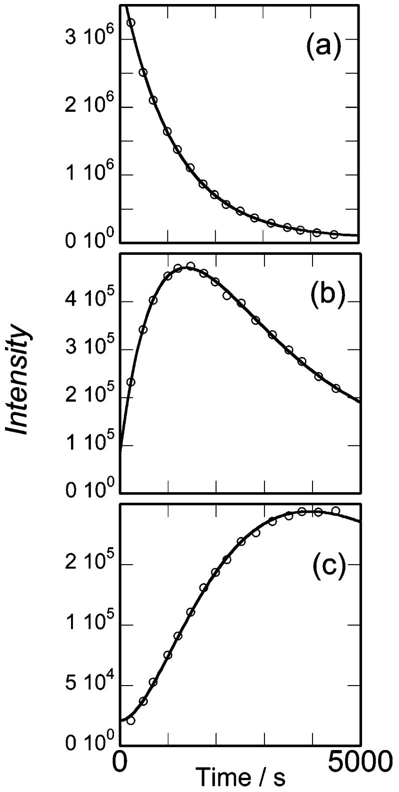


Figure 2. ^{1}H NMR signal intensities (arbitrary units) vs time for (a) MTO, (b) MTO-*d,* and (c) MTO-d_2 in benzene-d_6 at 298.0 K. Concentrations: 0.0175 mol kg^{-1} of MTO, 1.35 mol kg^{-1} of C_6D_5OD, 0.312 mol kg^{-1} of Lut. Curve fittings from eqs 1−3 correspond to (a) $k_\psi^{01} = 9.05 \times 10^{-4}$ s^{-1}, (b) $k_\psi^{12} = 5.77 \times 10^{-4}$ s^{-1}, and (c) $k_\psi^{23} = 2.47 \times 10^{-4}$ s^{-1}, with each rate constant relying on its predecessor(s), as explained in the text.

the rise and fall of the MTO-d_2 signal intensity with both k_ψ^{01} and k_ψ^{12} fixed. Pseudo-first-order conditions were maintained by using an excess amount of deuterium donor D over MTO; generally [D] > 60[MTO]. This inequality also disallows contributions from the reverse exchange processes. Typical data are presented in Figure 2.

Results

Preliminary Measurements. Suitable conditions were explored by recording the growth of the MTO-*d* triplet, which lies 6−7 Hz upfield of the MTO singlet. Exchange was not observed in neat deuterated organic solvents or in D_2O. A deuterium donor, methanol-d_4, was added to the sample solutions, and then they were divided into three portions. The first portion was used as is; trifluoroacetic acid-*d* was added to the second and pyridine-d_5 to the third. After 3 h at room temperature, a new triplet near the MTO singlet grew slowly only in the third sample. No H/D exchange was detected in neutral or acidified samples even at 323 K. A base is clearly required, but pyridine, which coordinates strongly to rhenium, proved to be a poor choice of base catalyst compared to those depicted in Chart 1.[6]

Most basic samples eventually became yellow, perhaps indicating a trace of MTO decomposition,[12,13,15,31] but the decomposition product(s) showed no kinetic or equilibrium effects. Neutral and acidified samples in D_2O gradually turned deep blue and finally deposited a dark blue gelatinous precipitate, an oligomer of $[MeRe^V(O)_2(H_2O)_2]$.[15,31,32]

Table 1. Equilibrium Constants at 298.0 K between MTO and Lewis Bases in Benzene-d_6

L	K_{ML}/kg mol^{-1}	pK_a^{a}	δ_{ML}
4-picoline	1710(240)	6.03	1.607
pyridine-d_5	425(22)	5.23	1.594
quinoline	37(5)	4.82	1.648^b
2-picoline	29.5(2)	5.95	1.592
methanol-d_4	1.01(6)	15.5	1.686^b
MeQ	0.18^c	5.42	(1.59)
Col	0.16^c	7.47	(1.59)
Lut	0.12^c	6.72	(1.59)
phenol-d_6	0.054^c	9.99	(1.59)

[a] Dissociation constant of conjugated acid of heterocyclic base LH^+, methanol, and phenol in water.[35−37] [b] δ_{obs} did not approach a plateau at a high concentration of L. [c] Calculated from eq 8 with δ_{ML} fixed at 1.59 (see text).

Adduct Formation in Benzene-d_6. MTO forms stable adducts with coordinating Lewis bases, MTO·L[33,34] (eq 4), as had been studied previously in nitromethane-d_3.[6] The same procedure was followed to

$$\text{MTO} + \text{L} = \text{MTO·L} \quad K_{ML} \tag{4}$$

evaluate K_{ML} in benzene-d_6. The notation L designates a Lewis base that coordinates to rhenium; the symbol B will be reserved for a Brønsted base that promotes H/D exchange. Addition of Lewis bases to MTO causes the chemical shift of MTO to move downfield in benzene-d_6. The MTO singlet remains sharp at any L/MTO ratio, owing to the high rate of eq 4. Thus, the observed chemical shift, δ_{obs}, is a concentration-weighted average of the chemical shifts of MTO with δ_{MTO} and MTO·L with δ_{ML}. The values of K_{ML} were calculated from eqs 5−7, in which the subscript T indicates the total concentration.

$$\delta_{obs} = \frac{\delta_{MTO} + K_{ML}[L]\delta_{ML}}{1 + K_{ML}[L]} \tag{5}$$

$$[L] = \frac{\sqrt{\xi^2 + 4K_{ML}[L]_T} - \xi}{2K_{ML}} \tag{6}$$

$$\xi = 1 + K_{ML}[MTO]_T - K_{ML}[L]_T \tag{7}$$

This treatment required a series of experiments with constant $[MTO]_T$; in this work it was maintained to within <4% during each titration. When L is a weak Brønsted base (i.e., pK_a(LH^+) >10) or its donor atom is sterically hindered, K_{ML} is too small to be determined from eqs 5−7 because the small extent of reaction prevents the resolution of $K_{ML}\delta_{ML}$ into its component values. In such cases, K_{ML} was calculated by assigning δ_{ML} as 1.59, a value found for bases that coordinate more strongly; this is a valid approach in that the value of δ_{ML} had been shown to be largely independent of the choice of L. Therefore, the denominator in eq 5 ap-

---

[31] Laurenczy, G.; Lukacs, F.; Roulet, R.; Herrmann, W. A.; Fischer, R. W. *Organometallics* **1996**, *15*, 848−851.

[32] Espenson, J. H.; Yiu, D. T. Y. *Inorg. Chem.* **2000**, *39*, 4113−4118.

[33] Herrmann, W. A. *J. Organomet. Chem.* **1995**, *500*, 149−174.

[34] Herrmann, W. A.; Kühn, F. E. *Acc. Chem. Res.* **1997**, *30*, 169−180.

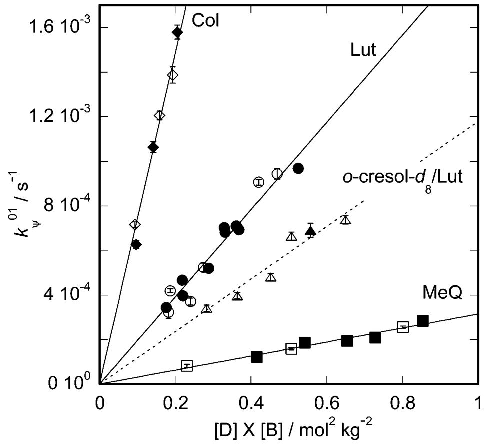


Figure 3. Pseudo-first-order rate constants, $k_\psi{}^{01}$, for H/D exchange of MTO as a function of [B] and [D] in benzene-d_6. The solid lines show $k_\psi{}^{01}$ with D = C_6D_5OD and the indicated base catalysts. The dashed line refers to the system *o*-cresol-d_8/Lut. Solid symbols, [D] = 1.0 mol kg^{-1}; open symbols, [D] = 0.5−1.4 mol kg^{-1}.

proaches unity ($1 \gg K_{ML}[L]$), giving eq 8. Table 1 lists the values of K_{ML}.

$$\delta_{obs} = \delta_{MTO} + K_{ML}[L]\delta_{ML} \tag{8}$$

Measurements of the H/D Exchange Rate Constants. Preliminary measurements showed that MTO·L exchanges H and D on methyl group little if at all. To focus on MTO itself, therefore, the use of sterically hindered, weakly coordinating bases was essential. Exchange between MTO and phenol-d_6 in benzene-d_6 was investigated by using the three bases shown in Chart 1. In benzene-d_6 other deuterium donors such as *o*-cresol-d_8 and methanol-d_4 with Lut as the base were used. (Because phenol is a weak acid, the extent of proton transfer from phenol-d_6, pK_a = 9.99, to Lut, pK_a(LutH$^+$) = 6.82, is negligible.) Rate constants were also determined in chloroform-*d*, acetone-d_6, and acetonitrile-d_3 with phenol-d_6 and Lut. Additional measurements were made in acetone-d_6 with phenol-d_6 and MeQ.

Reactions in Benzene-d_6. The observed rate constants for the first stage of H/D exchange, $k_\psi{}^{01}$, were directly proportional to both phenol-d_6 and base concentrations (eq 9). In eq 9, the deuterium donor and base

$$k_\psi{}^{01} = k_a\kappa[D][B] \tag{9}$$

are designated D and B, and the overall third-order rate constant is designated as $k_a\kappa$ for the sake of consistency with subsequent notation. Values of $k_a\kappa/10^{-3}$ kg^2 mol^{-2} s^{-1} with phenol-d_6 as the deuterium donor are as follows: MeQ, 0.315(7); Lut, 1.96(4); and Col, 7.42(15). The *o*-cresol-d_8/Lut pair also follows eq 9, with $k_a\kappa/10^{-3}$ kg^2 mol^{-2} s^{-1} = 1.18(4). The results are depicted in Figure 3.

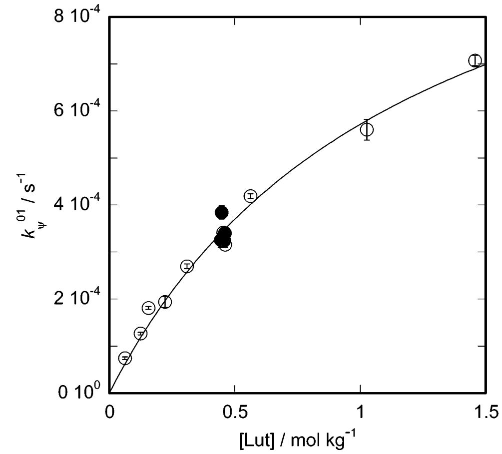


Figure 4. Pseudo-first-order rate constants for H/D exchange of MTO as a function of [Lut] with CD_3OD in benzene-d_6. Open circle, [CD_3OD] = 1.0 ± 0.1 mol kg^{-1}; solid circle (five points), [CD_3OD] = 0.31−1.41 mol kg^{-1}.

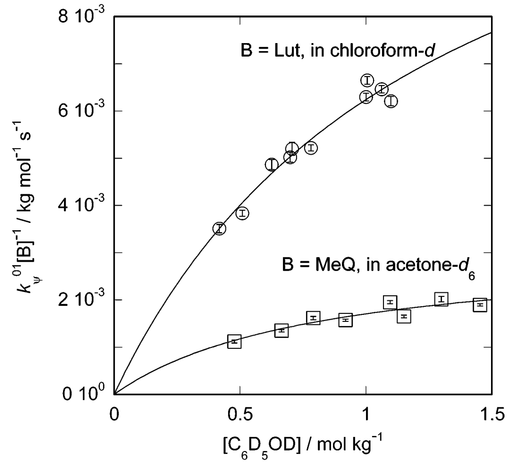


Figure 5. Illustrating kinetic saturation with respect to [C_6D_5OD] for B = Lut (0.13−0.28 mol kg^{-1}) in chloroform-*d* and B = MeQ (0.19−0.38 mol kg^{-1}) in acetone-d_6 at 298.0 K. The ordinate shows $k_\psi{}^{01}$/[B], each reaction being first-order with respect to [B].

With D = methanol-d_4 and B = Lut, values of $k_\psi{}^{01}$ are independent of methanol-d_4 concentration to 1.5 mol kg^{-1} but increase slightly at 1.5−4 mol kg^{-1}, where the medium is in effect a mixed solvent. Data at methanol-d_4 concentrations >1.5 mol kg^{-1} were therefore ignored. As shown in Figure 4, kinetic saturation with respect to [Lut] was found. The rate constant is described by eq 10: $k_b/10^{-3}$ s^{-1} = 1.26(10) and K_c = 0.83(10) kg mol^{-1}.

$$k_\psi{}^{01} = \frac{k_b K_c[\text{Lut}]}{1 + K_c[\text{Lut}]} \tag{10}$$

Reactions in Other Solvents. Experiments were carried out in chloroform-*d*, acetone-d_6, and acetonitrile-d_3, with D = phenol-d_6 and B = Lut, MeQ. In each of the cases $k_\psi{}^{01}$ was directly proportional to the base concentration. The exchange rates show kinetic saturation with respect to [D] in two systems: B = Lut in chloroform-*d* and B = MeQ in acetone-d_6 (Figure 5). With B = Lut, the rates are independent of [D] in acetonitrile-d_3 and in acetone-d_6 (data not shown). The general equation is given by eq 11, the limiting form $k_\psi{}^{01} = k_1$[B] being realized when $1 \ll \kappa$[D]. Table 2 summarizes the pertinent kinetic equations and numerical values.

$$k_\psi{}^{01} = \frac{k_a\kappa[D][B]}{1 + \kappa[D]} \tag{11}$$

Table 2. Summary of Rate Laws and Rate Constants for H/D Exchange of MTO at 298.0 K in Different Solvents, Deuterium Donors, and Bases

solvent	donor/base	k_ψ^{01}	eq	kinetic params[a]
C_6D_6	C_6D_5OD/MeQ	$k_a\kappa[B][D]$	9[b]	$K_1K_2k_3 = 0.315(7)$
C_6D_6	C_6D_5OD/Lut	$k_a\kappa[B][D]$	9[b]	$K_1K_2k_3 = 1.96(4)$
C_6D_6	C_6D_5OD/Col	$k_a\kappa[B][D]$	9[b]	$K_1K_2k_3 = 7.42(15)$
C_6D_6	*o*-cresol-d_8/Lut	$k_a\kappa[B][D]$	9[b]	$K_1K_2k_3 = 1.18(4)$
C_6D_6	CD_3OD/Lut	$(k_bK_c[B])/(1 + K_c[B])$	10	$k_3 = 1.26(10)$,[c] $K_1K_2 = 0.83(10)$[c]
$CDCl_3$	C_6D_5OD/Lut	$(k_a\kappa[D][B])/(1 + \kappa[D])$	11	$K_1k_2 = 14.1(18)$, $k_3/k_{-2} = 0.79(17)$
$(CD_3)_2CO$	C_6D_5OD/Lut	$k_a[B]$	11[d]	$K_1k_2 = 12.2(3)$
$(CD_3)_2CO$	C_6D_5OD/MeQ	$(k_a\kappa[D][B])/(1 + \kappa[D])$	11[d]	$K_1k_2 = 3.1(5)$, $k_3/k_{-2} = 1.22(44)$
CD_3CN	C_6D_5OD/Lut	$k_a[B]$	11[d]	$K_1k_2 = 38.7(13)$

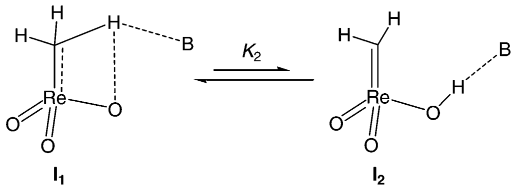
[a] The parameters are assigned according to eq 16, unless otherwise noted. K_1 is given in units of kg mol^{-1}, k_2 and k_{-2} in units of 10^{-3} s^{-1}, and k_3 in units of 10^{-3} kg mol^{-1} s^{-1}. [b] In the limit $1 \gg \kappa[C_6D_5OD]$; $\kappa = k_3/k_{-2}$. [c] k_3 and K_1K_2 are assigned according to eq 20. [d] In the limit $1 \ll \kappa[C_6D_5OD]$.

Table 3. Secondary Kinetic Isotope Effects for the H/D Exchange of MTO in Different Solvents with D = C_6D_5OD and B = Lut[a]

solvent	k^{01}:k^{12}:k^{23}
C_6D_6	1:0.89(3):0.87(6)
$CDCl_3$	1:0.90(10):0.71(10)
$(CD_3)_2CO$	1:0.90(3):0.75(7)
CD_3CN	1:0.88(4):0.54(4)

[a] k^{mn} corresponds to the relative rate constants for MTO-d_m to MTO-d_n.

Scheme 2. Structures Suggested for Intermediates



Secondary Kinetic Isotope Effects (KIE). As the H/D exchange reactions were studied under conditions in which the deuterium donor was used in excess, only the exchange of H by D was observed; therefore, primary kinetic isotope effects were not available. The experimental rate constants for each of the three steps were used to estimate secondary isotope effects. The rate constants were normalized by dividing the number of C−H bonds in MTO-d_n by $3 - n$; thus, $k^{01} = k_\psi^{01}/3$, $k^{12} = k_\psi^{12}/2$, $k^{23} = k_\psi^{23}$. The secondary KIE values for H/D exchange of MTO and phenol-d_6 with Lut in the four solvents are listed in Table 3. A direct comparison in this manner may include secondary equilibrium isotope effects (EIE) as well as KIE owing to the complex rate laws. Although H/D exchange grows slower at each step, the precision of the data does not allow a more penetrating analysis.

Discussion

General Reaction Scheme. The rate of exchange depends on the bases, deuterium donors, and solvents chosen. The reactions in eqs 12a and 12b can explain

$$\mathrm{MTO} + \mathrm{B} = \mathbf{I} \tag{12a}$$

$$\mathbf{I} + C_6D_5OD = \text{MTO-}d + \mathrm{B} + C_6D_5OH \tag{12b}$$

the kinetic data, other than that with methanol-d_4, discussion of which is being deferred to the next section. Equation 12a represents the formation of intermediate **I**; note that **I** is distinct from the trigonal-bipyramidal species MTO·L with a Re−N interaction. Whereas **I** participates directly in exchange, MTO·L lies off the pathway and, to the extent it forms, it inhibits exchange. As the MTO·L complexes do not undergo appreciable H/D exchange, it can be concluded that the interaction in **I** occurs not at rhenium but at a methyl proton. In our suggestion, the interaction between MTO and a base induces the keto/enol tautomerization of **I**, and the initially formed intermediate is assigned as $\mathbf{I_1}$ and the enol tautomer as $\mathbf{I_2}$. Neither intermediate, however, has been detected, as both species remain at very low concentrations throughout. The hypothetical structures are given in Scheme 2, and H/D exchange is described by eqs 13−15. Equation 13 represents coordination of

$$\mathrm{MTO} + \mathrm{B} = \mathbf{I_1} \quad K_1 \tag{13}$$

$$\mathbf{I_1} = \mathbf{I_2} \quad k_2/k_{-2} \tag{14}$$

$$\mathbf{I_2} + C_6D_5OD = \text{MTO-}d + \mathrm{B} + C_6D_5OH \quad k_3 \tag{15}$$

a base to the methyl proton of MTO. This step does not involve apparent bond breaking/forming; therefore, no significant energy barrier is expected. We will treat this step as a preequilibrium process. Equation 14 is the keto/enol tautomerization of MTO promoted by a base. This step presents a large structural change and thus will have a significant energy barrier. Equation 15 is the actual H/D exchange reaction between $\mathbf{I_2}$ and a deuterium donor. Taking eq 13 as the preequilibrium process and applying the steady-state approximation for $\mathbf{I_2}$, we can write the rate law as eq 16, where D is phenol-d_6 or *o*-cresol-d_8 and B the base. Comparison of this form

$$v_{\mathrm{ex}} = \frac{k_a[\mathrm{D}][\mathrm{B}][\mathrm{MTO}]}{1 + [\mathrm{D}]} = \frac{K_1k_2(k_3/k_{-2})[\mathrm{D}][\mathrm{B}][\mathrm{MTO}]}{1 + (k_3/k_{-2})[\mathrm{D}]} \tag{16}$$

with eq 11 shows that $k_a = K_1k_2$ and $\kappa = k_3/k_{-2}$. The variations among the experimental rate laws can be interpreted in terms of the limiting forms that are realized with different relative values of the constants in the denominator in eq 16. In benzene-d_6, the condition $k_{-2} \gg k_3[\mathrm{D}]$ allows simplification to $v_{\mathrm{ex}} = k_a\kappa[\mathrm{D}][\mathrm{B}][\mathrm{MTO}]$; therefore, $k_a\kappa = K_1k_2(k_3/k_{-2}) = K_1K_2k_3$. In chloroform-*d* with phenol-d_6 and Lut, or in acetone-d_6 with phenol-d_6 and MeQ, eq 16 can be applied as is. In acetone-d_6 and acetonitrile-d_3 with phenol-d_6 and

Lut, the condition $k_{-2} \ll k_3[\mathrm{D}]$ leads to a simplified equation, $v_{\mathrm{ex}} = k_{\mathrm{a}}[\mathrm{B}][\mathrm{MTO}]$; $k_{\mathrm{a}} = K_1k_2$. The observed rate and equilibrium constants under different conditions are listed in Table 2 with the appropriate rate laws.

Modified Reaction Scheme for Methanol-d_4. It is only reasonable to try to accommodate the data for D = methanol-d_4 and D = phenol-d_6 with the same model, eqs 13–15. There is one difference, however, that arises because methanol-d_4 is a considerably weaker Brønsted acid than phenol-d_6. Presumably, therefore, $k_3(\text{phenol-}d_6) \gg k_3(\text{methanol-}d_4)$. As a consequence, the interaction between Lut and MTO in eq 14 can be treated as a prior equilibrium. Were that the only factor, the rate law would be expressed as

$$v_{\mathrm{ex}} = \frac{K_1K_2k_3[\mathrm{Lut}][\mathrm{CD_3OD}][\mathrm{MTO}]}{1 + K_1K_2[\mathrm{B}]} \tag{17}$$

Additionally, however, further interactions must be considered. The nitrogen bases coordinate to the Re center of MTO, and methanol-d_4 may do so as well despite its weaker Lewis basicity (eq 18a). One must

$$\mathrm{CH_3ReO_3} + \mathrm{CD_3OD} = \underset{\alpha}{\mathrm{CH_3(O)_3Re\cdots O(D)CD_3}} \quad K_{18\mathrm{a}} \tag{18a}$$

$$\mathrm{CH_3ReO_3} + \mathrm{CD_3OD} = \underset{\beta}{\mathrm{O_3ReC(H)_2H\cdots O(D)CD_3}} \quad K_{18\mathrm{b}} \tag{18b}$$

also consider a separate interaction with the methyl proton of MTO (eq 18b). The two equilibria must be analyzed together, because the measurements do not distinguish them. In other words, the value of K_{ML} for methanol-d_4 given in Table 1 represents the sum $K_{\mathrm{ML}} = K_{18\mathrm{a}} + K_{18\mathrm{b}}$. Both α and β are dead-end intermediates, off the reaction pathway: α because we have shown that five-coordinated derivatives of MTO do not exchange; β because it is competitive with the formation of reactive intermediate $\mathbf{I_1}$ (eq 13). Thus, the expression for the reaction rate becomes more complex:

$$v_{\mathrm{ex}} = \frac{K_1K_2k_3[\mathrm{Lut}][\mathrm{CD_3OD}][\mathrm{MTO}]_{\mathrm{T}}}{(1 + K_1K_2[\mathrm{Lut}])(1 + K_{\mathrm{ML}}[\mathrm{CD_3OD}])} = \frac{K_1K_2k_3[\mathrm{Lut}][\mathrm{CD_3OD}][\mathrm{MTO}]_{\mathrm{T}}}{1 + K_1K_2[\mathrm{Lut}] + K_{\mathrm{ML}}[\mathrm{CD_3OD}] + K_1K_2K_{\mathrm{ML}}[\mathrm{Lut}][\mathrm{CD_3OD}]} \tag{19}$$

Because the rate was found to be independent of $[\mathrm{CD_3OD}]$, further simplification is required. The first two terms of the denominator are neglected for the sake of consistency with the experimental data, which gives

$$v_{\mathrm{ex}} = \frac{K_1K_2k_3[\mathrm{Lut}][\mathrm{MTO}]_{\mathrm{T}}}{K_{\mathrm{ML}} + K_1K_2K_{\mathrm{ML}}[\mathrm{Lut}]} \tag{20}$$

To reconcile eqs 10 and 20, the value of K_{ML} needs to be within experimental error of unity. Indeed, from Table 1, the value is 1.01 ± 0.06 kg mol^{-1}. Thus entirely by coincidence, eq 10 is a correct phenomenological description of the kinetics, for which eq 20 provides the full mathematical form.

Coordination Effects. The trigonal-bipyramidal species MTO·L are well-known; crystal structures of some have been reported.[38–40] The equilibrium constants K_{ML} are sensitive to steric and electronic effects. Steric effects aside, stronger Brønsted bases are also better Lewis bases: K_{ML} = 420 kg mol^{-1} for pyridine-d_5 (PyH$^+$, pK_{a} = 5.2) and 1700 kg mol^{-1} for 4-picoline (PicH$^+$, pK_{a} = 6.03). Steric hindrance reduces K_{ML}; values are 30 kg mol^{-1} for 2-picoline and 0.12 kg mol^{-1} for Lut. When steric effects predominate, K_{ML} becomes independent of basicity toward protons: values of pK_{a} (LH$^+$) increase as pyridine < 2-picoline < Lut < Col, whereas K_{ML} values decrease as pyridine > 2-picoline > Lut ≈ Col.

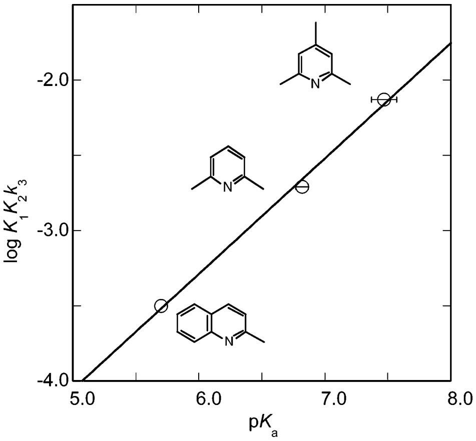


Figure 6. Plots of $\log(K_1K_2k_3)$ against the aqueous pK_{a} values of the protonated forms of the heterocyclic bases.

Rhenium–oxygen bonds in MTO·L adducts are weaker than those in MTO on the basis of structural data, which give Δd(Re–O) = 5–7 pm.[15,33] Infrared spectroscopy also shows weaker rhenium–oxygen bonds with O- or N-donating ligands.[40] Certain coordinating solvents such as THF-d_8 and DMSO-d_6 appear to form MTO·L adducts and decelerate exchange. The donor numbers of these solvents are 29.8 kcal mol^{-1} for DMSO and 20 kcal mol^{-1} for THF.[41]

Base Effects. Reaction 14 in benzene-d_6 represents O–H···N interactions because the bases do not coordinate appreciably to rhenium. The correlation between values of k_{a} (=$K_1K_2k_3$) with the pK_{a} values of BH$^+$ is shown in Figure 6; linear fitting gives a slope of +0.77(5). Because the value is large but less than unity, it can be inferred that intermediate $\mathbf{I_2}$ contains a substantially weakened O–H bond, but not fully deprotonated $[\mathrm{CH_2{=}ReO_3}]^-$. Given that a weak base such as MeQ forms $\mathbf{I_2}$, partially deprotonated MTO must be substantially stabilized by tautomerization, which plausibly affects the reactivity of $\mathbf{I_2}$.

Solvent Effects. The kinetics of exchange are sensitive to solvent, the major difference among them being

---

(35) Smith, R. M.; Martell, A. E. *Critical Stability Constants*; Plenum: New York, 1974.

(36) Lide, D. R., Ed. *CRC Handbook of Chemistry and Physics,* 81st ed.; CRC Press: Boca Raton, FL, 2000.

(37) Averaged pK_{a} values at ca. 298 K reported after 1980; data from Beilstein Commander.

(38) Herrmann, W. A.; Kuchler, J. G.; Weichselbaumer, G.; Herdtweck, E.; Kiprof, P. *J. Organomet. Chem.* **1989**, *372*, 351–370.

(39) Herrmann, W. A.; Kuchler, J. G.; Kiprof, P.; Riede, J. *J. Organomet. Chem.* **1990**, *395*, 55–67.

(40) Herrmann, W. A.; Correia, J. D. G.; Rauch, M. U.; Artus, G. R. J.; Kühn, F. E. *J. Mol. Catal. A* **1997**, *118*, 33–45.

(41) Marcus, Y. *Ion Solvation*; Wiley: Chichester, U.K., 1985.

their polarity; dielectric constants are as follows: benzene, 2.28; chloroform, 4.72; acetone, 20.7; acetonitrile, 35.95.[36] The rate laws with D = phenol-d_6 and B = Lut in each solvent were interpreted according to the relative values of terms in the denominator of eq 16: i.e., $k_{-2} \gg k_3[\mathrm{D}]$ in benzene-d_6; $k_{-2} \approx k_3[\mathrm{D}]$ in chloroform-d; $k_{-2} \ll k_3[\mathrm{D}]$ in acetone-d_6 or acetonitrile-d_3. Although the solvent dependence of the rate law does not allow a rigorous comparison of the rate constants among all solvents, the general trend indicates the accelerating effect of polar solvents. The faster reactions observed in more polar solvents suggest the intervention of charged or polarized intermediates. In a polar solvent such as acetonitrile-d_3, enolate-MTO might be produced by the deprotonation of MTO, whereas the partial deprotonation of MTO or the formation of a strong ion pair $\{[\mathrm{CH_2{=}ReO_3}]^-{\cdot}[\mathrm{HB}]^+\}$ might be favored in nonpolar solvents because charged species are substantially destabilized by the lack of solvation.[15,41,43]

Solvent effects on the basicity of the bases toward a proton in MTO should also be considered.[42] The ratio of the equilibrium constants for the deprotonation process in benzene-d_6 is $K_1K_2(\mathrm{Lut})/K_1K_2(\mathrm{MeQ}) = 4.4$. The ratio of the rate constants for the deprotonation process in acetone-d_6 is $K_1k_2(\mathrm{Lut})/K_1k_2(\mathrm{MeQ}) = 3.9$. (The ratio of K_1k_2 strongly reflects the deprotonation process, because acid/base neutralization reaction is rapid.) This ratio can be compared with the ratio of K_a in water: $K_a(\mathrm{LutH^+})/K_a(\mathrm{MeQH^+}) = 6$. The rough agreement indicates solvent effects on the basicity of bases are relatively small and the partial proton extraction from MTO occurs in both benzene-d_6 and acetone-d_6.

Donor Effects. The H/D exchange rate diminishes with increasing pK_a of the deuterium donor: phenol (9.99) > cresol (10.29) ≫ methanol (15) ≫ acetone (19). Acetone-d_6, a potential deuterium donor, did not exchange.

One might suspect that high concentrations of the deuterium donors would alter the dielectric constant of benzene-d_6 solutions. The activity coefficient of the proton and deuteron in a nonpolar solvent is likely to be increased by the addition of polar reagents such as phenol-d_6 ($\epsilon = 12$). To explore this matter, isodielectric measurements were carried out by adding benzyl alcohol ($\epsilon = 10$) at a concentration, together with phenol-d_6, such that [benzyl alcohol] + [phenol-d_6] = 1.3 mol kg^{-1}. The experiment failed, however, because benzyl alcohol itself seems to coordinate to MTO, thus reducing the H/D exchange reactivity.

The rate constant difference between reactions with phenol-d_6 and o-cresol-d_8 shows the absence of medium effects, whereas the reaction with methanol-d_4 implies otherwise. The third-order rate constants measured with D = phenol-d_6 and o-cresol-d_8 in benzene-d_6 represent the product $K_1K_2k_3$. Because the K_1K_2 step is common to both, the data reflect the relative values of k_3. The ratio of the rate constants with phenol-d_6 and o-cresol-d_8 was 1.66, which roughly agrees with the K_a ratio between phenol and o-cresol: $K_a(\mathrm{phenol})/K_a(\mathrm{cresol}) = 1.99$. Considering the use of aqueous pK_a values and their experimental errors, this can be taken as good agreement. Thus, k_3 directly reflects the heterolytic O−D bond energy of phenol-d_6 and o-cresol-d_8.

The value $K_1K_2k_3$ for D = methanol-d_4 can be also calculated from the separately estimated K_1K_2 and k_3. The value $10^3K_1K_2k_3(\text{methanol-}d_4/\mathrm{Lut}) = 1.0$ kg^2 mol^{-2} s^{-1} is close to $10^3K_1K_2k_3(o\text{-cresol-}d_8/\mathrm{Lut}) = 1.2$ kg^2 mol^{-2} s^{-1}, despite their pK_a difference. Because methanol-d_4 is as polar ($\epsilon = 32.6$) as acetonitrile, methanol-d_4 in the bulk, which is 60 times in excess of MTO, may stabilize the intermediates by specific solvation.

Reaction Coordinate Diagram. In this study, we found that H/D exchange depends on the solvents, bases, and deuterium donors. The formation of partially deprotonated MTO as the intermediate is facilitated by a strong Brønsted base. The pK_a of a deuterium donor will directly affect the activation barrier of H/D exchange. The solvent may affect both the stability of the intermediate and the activation barrier for H/D exchange. Because H/D exchange directly reflects the pK_a of the deuterium donor, a lower activation barrier is expected in polar solvents compared with that in nonpolar solvents.

A reaction coordinate diagram of H/D exchange for MTO is illustrated in Scheme 3; obviously it is nearly symmetric for H/D exchange. In the beginning MTO exists exclusively in the keto form because of the large energy difference between keto- and enol-MTO. A base present in solution interacts with MTO at the Re center or at the methyl proton. Without steric hindrance, the base interacts with the Re center of MTO to form a trigonal-bipyramidal compound, which prevents keto/enol tautomerization and, therefore, H/D exchange. A base with a steric barrier initially interacts with MTO at the methyl proton to form intermediate **I$_1$** with the weakened C−H bond. This partial deprotonation of MTO facilitates its keto/enol tautomerization. The base-promoted enol isomer **I$_2$** or the strong ion pair $\{[\mathrm{CH_2{=}ReO_3}]^-{\cdot}[\mathrm{BH}]^+\}$ is a reactive intermediate for subsequent H/D exchange. The H/D exchange takes place via an interaction between **I$_2$** and the deuterium donor to form the activated complex. In Scheme 3 we depicted the activated complex, which still requires the old O−H/O−D bonds to break and the new O−D/O−H bonds to form. Clearly, the heterolytic O−D bond energy of a deuterium donor has a strong influence in this process; however, the stability and reactivity of **I$_2$** also depend on the nature of a base and a solvent. The sequence as written contains several rapid steps that have been postulated; not every one was capable of independent verification. The deuterated intermediate ***I$_2$-d*** produces deuterated MTO, by the dissociation of base. With an excess deuterium donor the reaction sequence will be repeated until the three protons of MTO are exchanged.

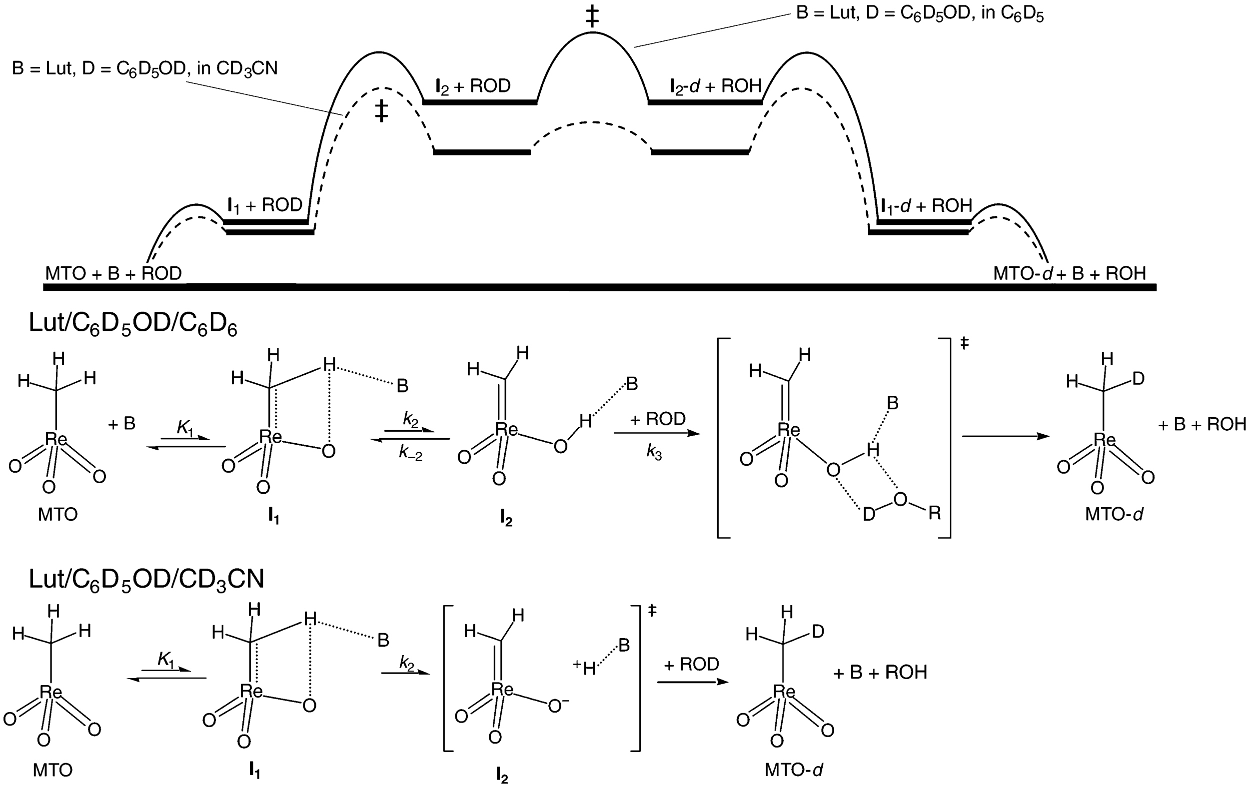
In acetonitrile-d_3, a noncoordinating polar solvent, the deprotonated intermediate **I$_2$** can be stabilized by solvation. This enolate-MTO facilitates the access to the transition state and therefore lowers the activation barrier for H/D exchange. Consequently, the formation of **I$_2$** becomes the rate-determining step for B = Lut, in acetonitrile-d_3 or in acetone-d_6. On the other hand, a weaker base cannot produce the reactive enolate-MTO;

---

(42) Popovych, O.; Tomkins, R. P. T. *Nonaqueous Solution Chemistry*; Wiley-Interscience: New York, 1981.

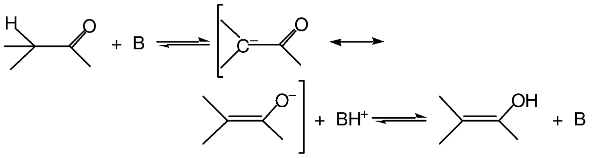
(43) Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*, 2nd ed.; VCH: Weinheim, Germany, 1988.

Scheme 3. Reaction Coordinate Diagram for H/D Exchange of MTO

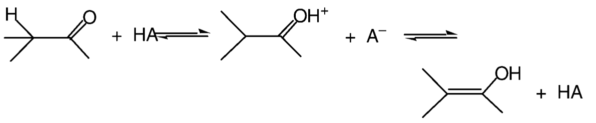


therefore, the higher energy barrier remains the subsequent H/D exchange step as for B = MeQ in acetone-d_6.

Absence of Acid Catalytic Reaction. Acids and bases catalyze the H/D exchange of ketones, as shown in eqs 21 and 22.[7] As for MTO, even pyridine (the pK_a of PyH^+ is 5.23) catalyzes slow H/D exchange of MTO and the bases in Chart 1 do so more efficiently, whereas trifluoroacetic acid does not.



(21)



(22)

The lack of catalytic ability of acids might be rationalized by the characteristic rhenium–oxygen bond in MTO. Despite the fact that members of the L–ReO_3 family (L = η^5-C_5Me_5, HB(pz)$_3$, σ-Mes, CH_3) have quite similar rhenium–oxygen bond lengths,[44–47] the oxygens in MTO in particular have a low electron density compared to the oxygens in the other compounds.[48] The three oxo ligands in MTO donate electron density to the rhenium center to compensate for electron deficiency at the metal center, which disfavors the cationic intermediate $CH_3ReO_3H^+$. In base catalysis, on the other hand, nucleophilic attack on the methyl proton forms a negatively charged intermediate, which can distribute electron density to the rhenium–oxygen moiety, stabilizing the enol. The perrhenate ion also has a rhenium–oxygen bond length near those of L–ReO_3 complexes,[49,50] but its ^{17}O NMR resonance appears at a higher field.[48] The distribution of the negative charge over four oxygen atoms is suggested for this phenomenon.[51]

The absence of H/D exchange for the trigonal-bipyramidal species MTO·L also implies the importance of the electronic deficiency of the –ReO_3 moiety for the keto/enol tautomerization of MTO. The formation of MTO·L eases the electronic deficiency of the Re center prior to the deprotonation; hence, the deprotonation loses the advantage of stabilizing a negatively charged intermediate for MTO·L. As a result, the MTO·L formation inhibits the access to keto/enol tautomerization.

Kinetic Isotope Effects. Secondary kinetic isotope effects are usually small, $k_H/k_D = 0.7–1.5$, because C–H bond cleavage is not directly involved in a reaction.[52] The sources of the secondary KIE are the steric differ-

---

(44) Herrmann, W. A.; Ladwig, M.; Kiprof, P.; Riede, J. *J. Organomet. Chem.* **1989**, *371*, C13–C17.

(45) Okuda, J.; Herdtweck, E.; Herrmann, W. A. *Inorg. Chem.* **1988**, *27*, 1254–1257.

(46) Herrmann, W. A.; Okuda, J. *J. Mol. Catal.* **1987**, *41*, 109–122.

(47) Herrmann, W. A.; Romao, C.; Fischer, R. W.; Kiprof, P.; De Meric de Bellefon, C. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 185–187.

(48) Herrmann, W. A.; Kiprof, P.; Rypdal, K.; Tremmel, J.; Blom, R.; Alberto, R.; Behm, J.; Albach, R. W.; Bock, H.; Solouki, B.; Mink, J.; Lichtenberger, D.; Gruhn, N. E. *J. Am. Chem. Soc.* **1991**, *113*, 6527–6537.

(49) Lock, C. J. L.; Turner, G. *Acta Crystallogr., Sect. B* **1975**, *B31*, 1764–1765.

(50) Krebs, B.; Hasse, K. D. *Acta Crystallogr., Sect. B* **1976**, *B32*, 1334–1337.

(51) Herrmann, W. A.; Kühn, F. E.; Roesky, P. W. *J. Organomet. Chem.* **1995** *485*, 243–251.

(52) Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry,* 4th ed.; Kluwer Academic/Plenum: New York, 2000.

ences of a C−H(D) bond, the differences in hyperconjugative stabilization arising from C−H(D) bond strengths, and the electronegativity differences of H and D.

In our study, large errors of the KIE values and the complex rate laws prevent a detailed quantitative analysis of isotope effects. However, the general trend is found to be $k^{01} > k^{12} > k^{23}$; that is, the replacement of a proton in MTO with a deuteron decelerates H/D exchange. From this trend, we infer that the heavier deuterium atom hinders the twist motion of sp^3 to sp^2 during tautomerization. Stabilization from hyperconjugation may be reduced because a proton is slightly more electronegative than a deuteron.[53,54] This analysis of the KIE also supports the involvement of the enol-MTO intermediate.

Acknowledgment. This research was supported by the National Science Foundation (Grant No. CHE-020409). Some experiments were conducted with the use of the facilities of the Ames Laboratory, which is operated by Iowa State University of Science and Technology under contract W-7405-Eng-82 with the U.S. Department of Energy.

OM049029S

---

(53) Alston, W. C., II; Haley, K.; Kanski, R.; Murray, C. J.; Pranata, J. *J. Am. Chem. Soc.* **1996**, *118*, 6562−6569.

(54) Kovach, I. M.; Hogg, J. L.; Raben, T.; Halbert, K.; Rodgers, J.; Schowen, R. L. *J. Am. Chem. Soc.* **1980**, *102*, 1991−1999.