Theoretical Study of the Rate Constants and Kinetic Isotope Effects of the 1,2-Hydrogen-Atom Shift of Methoxyl and Benzyloxyl Radicals Assisted by Water

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Rate constants and kinetic isotope effects for the 1,2-H shift of methoxyl and benzyloxyl radicals were studied in the presence of water molecules. The electronic structure calculations were carried out at the UB3LYP/6-31G* level, and the dynamics calculations were performed using the variational transition state theory with semiclassical multidimensional corrections for tunneling. The study deals with 1:1 and 1:2 radical−water complexes in the gas phase. It was found that water catalyzes these rearrangement reactions by forming a bridge containing two water molecules. The dynamics calculations show that the methoxyl−water complexes react only very slowly. The rate constants for 1:2 complexes with the benzyloxyl radical are in relative good agreement with the results of laser flash photolysis. The kinetic isotope effects calculated using heavy water indicate that tunneling makes an important contribution in the 1:1 complex, whereas the contribution due to vibrations is more important for the 1:2 complexes. In both cases, the kinetic isotope effects are substantial. It is concluded that the 1,2-H shift for both radicals is catalyzed by two water molecules through a mechanism that involves the formation of a preliminary 1:1 complex.

1. Introduction

Alkoxyl radicals, RCH_2O, play an important role as intermediate species in atmospheric and combustion reactions.[1−3] For instance, they are involved in oxidation reactions with molecular oxygen and in isomerization reactions of degradation of heavier alkoxyl radicals.[4,5] The rearrangement of primary alkoxyl radicals, RCH_2O, to ketyl radicals, RCHOH, may be important biologically because alkoxyl radicals are highly reactive. If this 1,2-H-atom shift is slow, it could lead to oxidative damage. On the contrary, the ketyl radical and its anion products of this rearrangement are poor oxidizing agents, and it is unlikely that they would cause damage to biological targets. In this connection, Ingold et al.[6] invented the first superoxide thermal source, bis(4-carboxybenzyl)hyponitrite (SOTS-1), which can be used in studies on the effects of superoxide in biologically relevant systems. The generation of superoxide from SOTS-1 and its derivatives involves a 1,2-H shift reaction, which thermal rate constants were measured by laser flash photolysis (LFP) by Konya et al.[7] Early EPR studies of the 1,2-H shift were done in aqueous solution,[8−10] and it was simply assumed that water was essential for the 1,2-H shift to occur. Later, Elford and Roberts[11] by the same technique proved that this reaction can also be assisted by alcohols. Specifically, they observed that at 220 K in the presence of ethanol, and in cyclopropane as a solvent, the allyloxyl radical, $H_2C{=}CH{-}CH_2O$, rearranges to the 1-hydroxylallyl $H_2C{=}CHCHOH$ radical. However, the ethoxyl radical, CH_3CH_2O, did not undergo a 1,2-H shift, probably because the ketyl radical product does not benefit from allylic stabilization. Konya et al.[7] generated benzyloxyl ($PhCH_2O$) and 4-ethoxy-carbonylbenzyloxyl ($EtOC(O)C_6H_4CH_2O$) radicals from SOTS-1 derivatives, using dried acetonitrile as solvent and water and different alcohols as catalysts, as an intermediate in the generation of superoxide radical. The authors made also an estimate of the pseudo-first-order rate constant at room temperature of the 1,2-H shift of both radicals in dry acetonitrile catalyzed by water, obtaining rate constants of about 2×10^8 s^{-1}. They also observed that the pseudo-first-order rate constant of the rearrangement using 2-propanol as catalyst is independent of whether dried acetonitrile or dried benzene were employed as solvents. From those LFP experiments, the authors concluded that only hydroxylic compounds catalyze the rearrangement and that only one hydroxylic group participates in the rearrangement.

To get an insight into the role played by water and alcohols in the 1,2-H shifts of alkoxyl radicals, we have studied the gas-phase 1,2-H rearrangements of methoxyl and benzyloxyl radicals catalyzed both by one and by two water molecules. Specifically, we evaluate the pseudo-first-order thermal rate constants of these complexes at room temperature using the variational transition state theory with multidimensional corrections for tunneling (VTST/MT)[12] together with density funtional theory methods (DFT). The incorporation of quantum effects is especially important because all reactions involve the transfer of one or more hydrogen atoms, which are light particles and therefore susceptible to tunneling. By using these tools, the objectives of this paper are, from one side, to analyze the differences between the 1,2-H shifts in methoxyl and benzyloxyl radicals because it is known that the methoxyl radical does not rearrange on the EPR time scale and, from the other side, to establish mechanism of catalysis.

Another important aspect of the 1,2-H shift is the kinetic isotope effect (KIE). Elford and Roberts[11] found a very complicated KIE behavior for the rearrangement of the 1-hydroxylallyl radical using cyclopropane as solvent and EtOD as a deuterated catalyst. By using the complexes mentioned above, it is difficult to mimic the KIEs obtained in solution because the reaction may follow more than one mechanism. However,

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these gas-phase complexes can be quite useful in the study of the behavior of the KIEs when the solvent is nonpolar (for instance, benzene) and at low concentrations of the deuteration agent. Thus, we also evaluate KIEs by using the VTST/MT method when the gas-phase rearrangement takes place by specific solvation of heavy water.

2. Theoretical Background

We applied the canonical variational transition state theory (CVT)[12,13] to evaluate the pseudo-first-order hydrogen transfer rate constants. The CVT rate constant, k^{CVT}, is defined as the least forward flux of trajectories that cross the surface perpendicular to the minimum energy path(MEP), at a given temperature T

$$k^{\mathrm{CVT}}(T) = \min k^{\mathrm{GT}}(T, s) \tag{1}$$

In this equation, $k^{\mathrm{GT}}(T,s)$ is the generalized transition state theory rate constant at the dividing surface that intersects the MEP at s:

$$k^{\mathrm{GT}}(T, s) = \frac{\sigma}{h\beta}\frac{Q^{\mathrm{GT}}(T, s)}{Q^{\mathrm{R}}(T)}\exp[-\beta V_{\mathrm{MEP}}(s)] \tag{2}$$

where σ is the symmetry factor, $\beta = (k_{\mathrm{B}}T)^{-1}$, k_{B} is the Boltzmann constant, $Q^{\mathrm{GT}}(T, s)$ and $Q^{\mathrm{R}}(T)$ are the total partition functions of the reactant and generalized transition state, respectively, and V_{MEP} is the potential energy of the MEP at s. If the forward flux is minimized at the transition state ($s = 0$), there is no variational effects and the CVT rate constant equalizes the conventional transition state rate constant (TST).

Tunneling effects are incorporated in the CVT rate constant through a ground-state multidimensional transmission factor $\kappa^{\mathrm{G}}(T)$, which is defined as the ratio between the thermally averaged ground-state semiclassical probability $P^{\mathrm{G}}(E)$ and the thermally averaged classical probability $P_{\mathrm{cl}}(E)$:

$$\kappa^{\mathrm{G}}(T) = \frac{\int_0^\infty P^{\mathrm{G}}(E)\mathrm{e}^{\beta \mathrm{E}}\,\mathrm{d}E}{\int_0^\infty P_{\mathrm{cl}}(E)\,\mathrm{d}E} \tag{3}$$

The classical probability is zero below the classical barrier height and unity otherwise. The semiclassical probability, $P^{\mathrm{G}}(E)$, evaluated along the MEP without taking into account the curvature among the reaction path and the transverse modes, leads to the zero-curvature transmission factor for tunneling,[12] κ^{ZCT}. The curvature can be taken into account by using the centrifugal-dominant small curvature semiclassical adiabatic ground-state tunneling approximation,[14] κ^{SCT}, which is appropriate for systems with small to intermediate reaction path curvature. If we use the SCT transmission factor for tunneling, the final computed rate constant $k^{\mathrm{CVT/SCT}}$ is expressed as the product of the classical rate and the semiclassical transmission factor

$$k^{\mathrm{CVT/SCT}}(T) = \kappa^{\mathrm{SCT}}(T)k^{\mathrm{CVT}}(T) \tag{4}$$

The kinetic isotope effects for the different complexes studied

$$\eta_{\mathrm{t}} = k_{\mathrm{H}}^{\mathrm{CVT/SCT}}(T)/k_{\mathrm{D}}^{\mathrm{CVT/SCT}}(T) \tag{5}$$

were factorized as

$$\eta_{\mathrm{t}} = \eta_{\mathrm{var}}\eta_{\mathrm{rot}}^{\ddagger}\,\eta_{\mathrm{vib}}^{\ddagger}\eta_{\mathrm{tun}} \tag{6}$$

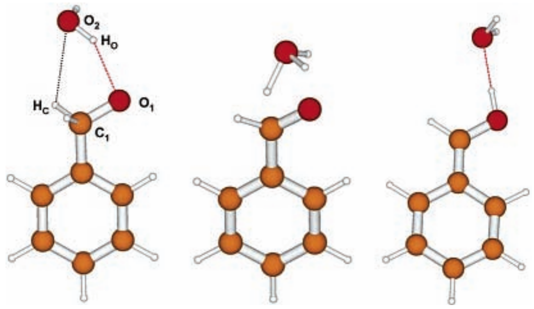

Figure 1. Initial (R), transtion state (TS), and final (P) configurations for the 1,2-H atom shift of the 1:1 benzyloxyl−water complex. Numbering as in Table 1.

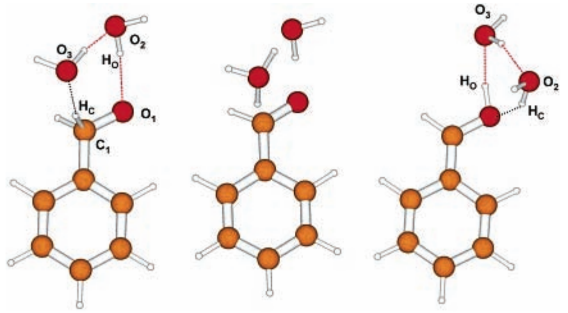

Figure 2. Same as Figure 1 but for the 1:2 complex.

where $\eta_{\mathrm{var}} = \mathrm{KIE}^{\mathrm{CVT}}/\mathrm{KIE}^{\mathrm{TST}}$ is the ratio of KIEs between variational and conventional transition states theories, $\eta_{\mathrm{rot}}^{\ddagger}$ and $\eta_{\mathrm{vib}}^{\ddagger}$ are KIEs due to rotation and vibration (taking as reference the transition state), respectively, and $\eta_{\mathrm{tun}} = \kappa_{\mathrm{H}}^{\mathrm{SCT}}/\kappa_{\mathrm{D}}^{\mathrm{SCT}}$.

3. Computational Details

All of the stationary points for the methoxyl and benzyloxyl radicals with one (1:1 complexes) and two water molecules (1:2 complexes) were fully optimized at the density functional theory unrestricted Becke's 3 parameter functional (UB3LYP) level,[15] with the 6-31G* basis set. This level of theory was chosen based on the calculations of the 1,2-hydrogen shift from hydrogen peroxide to water oxide assisted by one and two water molecules carried out by Okajima.[16] This author used the B3LYP/6-31++G** level of calculation but indicated that neither the diffuse functions (+) nor the polarization functions (*) had much effect on the energetics of the reaction. Because our systems have some similarities to those studied by Okajima, we used the 6-31G* basis set. As a further test, we also optimized the 1:1 complexes with the methoxyl radical at the UB3LYP/6-31++G** level with a difference in the barrier height compared to the UB3LYP/6-31G* level of only 0.2 kcal mol^{-1}.

The 1:1 and 1:2 complexes for the benzyloxyl radical rearrangement are depicted in Figures 1 and 2, respectively. Similar structures were studied for the rearrangement of the methoxyl radical. Starting from the transition state, the MEP was constructed at the UB3LYP/6-31G* level by following the Page−McIver algorithm[17] using a local quadratic approximation and with a stepsize of 0.01 a_0 amu$^{1/2}$ and Hessian calculations every 0.1 a_0 amu$^{1/2}$. This stepsize was small enough to obtain converged values of the thermal rate constants. The same procedure was applied to the 1:1 and 1:2 heavy water complexes of both radicals. With this information along the MEP, it is possible to calculate the curvature along this path and the ground-state transmission factors within the small-curvature method for tunneling.

TABLE 1: Main Distances (in Å) Involved in the 1,2-H Shift of Methoxyl and Benzyloxyl Radicals with One and Two Water Molecules, Respectively[a]

	R	TS	P	R	TS	P
	Methoxyl·1H_2O			Benzyloxyl·1H_2O		
C_1O_1	1.374	1.322	1.363	1.362	1.319	1.355
O_1H_O	1.996	1.336	0.981	1.998	1.416	0.982
O_2H_O	0.975	1.152	1.836	0.975	1.103	1.787
O_2H_C	2.606	1.259	0.971	2.579	1.267	0.970
C_1H_C	1.100	1.475	3.568	1.109	1.485	4.026
	Methoxyl·2H_2O			Benzyloxyl·2H_2O		
C_1O_1	1.364	1.322	1.353	1.351	1.315	1.362
O_1H_O	1.849	1.319	0.995	1.837	1.451	0.995
O_2H_O	0.984	1.136	1.739	0.985	1.068	1.721
O_2H_W	1.815	1.244	0.990	1.794	1.345	0.989
O_3H_W	0.987	1.197	1.790	0.989	1.201	1.816
O_3H_C	2.037	1.232	0.986	1.954	1.181	0.980
C_1H_C	1.126	1.437	2.138	1.141	1.519	2.905

[a] Numbering as in Figures 1 and 2. The letters R, TS, and P stand for reactant, transition state, and product, respectively.

All of the quantum-chemical calculations were carried out with the Gaussian 98 suite of programs[18] and the dynamics calculations were performed with Polyrate 8.5[19] and Gaussrate 8.5[20] programs.

4. Results and Discussion

The main distances obtained at the UB3LYP/6-31G* corresponding to the 1,2-H shift in the 1:1 and 1:2 complexes with methoxyl and benzyloxyl radicals are listed in Table 1. The O_2H_C distance of the initial configuration is large in the 1:1 complexes, indicating a weak hydrogen bond interaction. This interaction is more favorable between H_O and O_1 atoms with distances about 2 Å in both methoxyl and benzyloxyl complexes. The distances between the water molecule and the radicals decrease substantially in the transition state to aid the double hydrogen transfer, bringing the H_C and H_O hydrogen atoms closer to the water molecule. After the transfer, the water molecule separates from the C_1 carbon atom and forms a strong hydrogen bond with the hydroxyl group. In the 1:2 complexes, the O_3H_C and O_1H_O distances are shorter than the O_2H_C and O_1H_O distances in the 1:1 complexes in the initial configuration, which is due to a better positioning of the water molecules, helping to form stronger hydrogen bonds. The H_C and H_O transferred hydrogens are closer to the water molecules in the transition state of the 1:2 complexes regarding to the 1:1 complexes indicating an asynchronous motion of the transferred hydrogens, which is more accentuated in the case of the benzyloxyl radical. Thus, the hydrogen that moves the most between the reactant and the transition state is H_C, the H_W hydrogen atom is about halfway between the two water molecules, whereas H_O is the hydrogen that moves the most between the transition state and the product. The formation of the ketyl radicals in the 1:2 complexes is accompanied by a large rearrangement of the water molecule that initially is positioned close to the C_1 carbon atom. This water molecule, after the hydrogen is transferred, moves toward the O_1 oxygen atom to form hydrogen bonds with the hydroxylic group and with the other water molecule, which provides more stabilization to the product than in the corresponding 1:1 complexes.

As shown in Table 2, the participation of one water molecule in the reaction reduces substantially the barrier height, which indicates that water acts as a catalyst for this reaction. The structural changes that imply the incorporation of a second molecule in the reaction, such as the formation of stronger hydrogen bonds between the water molecules and the alkoxyl radicals, are reflected in the barrier heights. Thus, in the 1,2-H shift catalyzed by one water molecule, the barrier height is reduced by about half when the second water molecule is incorporated into the reaction. Therefore, from the static point of view, the 1,2-H shift in both radicals is catalyzed by water and is more favorable when two water molecules participate in the reaction.

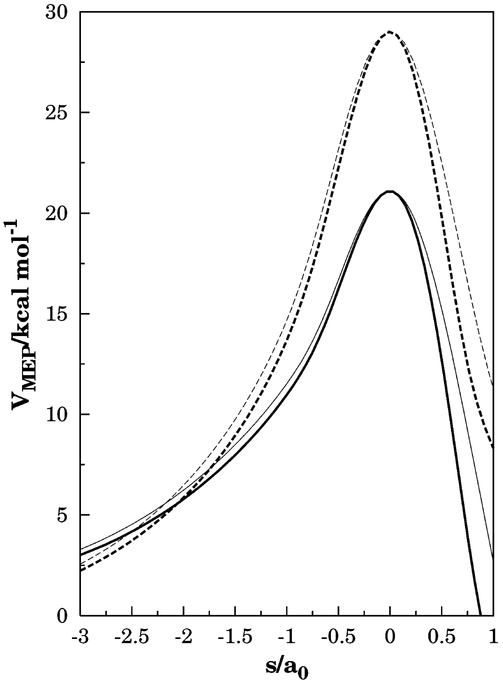

Figure 3. Plot of the minimum energy path for the 1:1 complexes: methoxyl·H_2O (thick-dashed line), methoxyl·D_2O (thin-dashed line), benzyloxyl·H_2O (thick-continuous line), and benzyloxyl·D_2O (thin-continuous line).

TABLE 2: Barrier Height, V_0, and Energy Difference between the Initial and Final States, ΔE, in kcal mol^{-1}, Evaluated at the UB3LYP/6-31G* Level for the 1,2-H Shift of Methoxyl/Benzyloxyl Radicals with Water Molecules

water molecules	V_0	ΔE
0	38.1/28.9	−1.0/−15.4
1	29.0/21.1	−3.5/−19.0
2	17.2/10.9	−5.9/−20.4

The dynamics aspects of the 1,2-H shift reactions were studied, as mention in section 2, by using the variational transition state theory with multidimensional semiclassical corrections for tunneling. The MEP for the 1:1 and 1:2 complexes are depicted in Figures 3 and 4, respectively. On the basis of the information along the MEP, it is possible to evaluate the CVT/SCT rate constants, for which values for the 1:1 and 1:2 complexes of methoxyl and benzyloxyl radicals with light and heavy water are listed in Table 3 at room temperature. The tunneling transmission factors are substantially larger for the 1:1 complexes, which is expected because these barriers are larger and sharper than for the 1:2 complexes and only involve the motion of two hydrogen atoms. The SCT transmission factors are larger than the ZCT transmission factors because of the curvature along the reaction path. Although the tunneling contribution is more important for the 1:1 complexes, the rate constants for the 1:2 complexes are about 6 orders of magnitude larger than for the 1:1 complexes because of the differences in the barrier heights. At room temperature, the 1:1 and 1:2 complexes with methoxyl radicals have rate constants of 3.63×10^{-5} and 7.00×10^{2} s^{-1}, respectively. These values

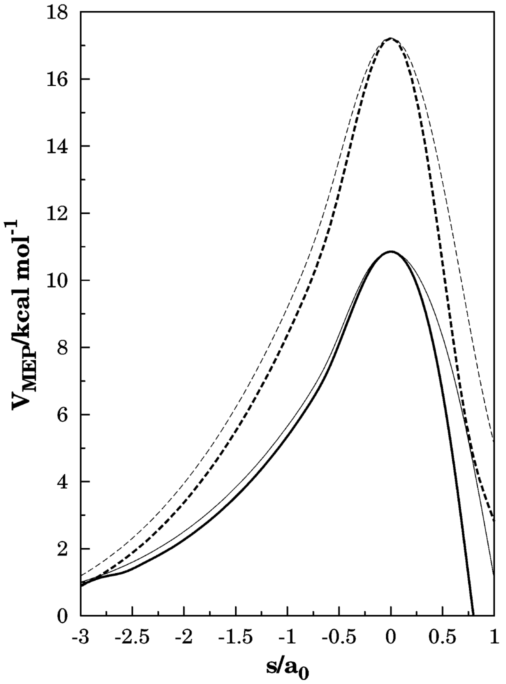

Figure 4. Same as Figure 3 but for the 1:2 complexes.

TABLE 3: Values of the Tunneling Transmission Factors, κ^{ZCT} and κ^{SCT} and TST, CVT, and CVT/SCT Rate Constants (in s^{-1}), Respectively, for the 1,2-H Shift of Methoxyl (M) and Benzyloxyl (B) Radicals Assisted by Root and Deuterated Water Molecules at $T = 300$ K

system	κ^{ZCT}	κ^{SCT}	k^{TST}	k^{CVT}	$k^{CVT/SCT}$
M·1H_2O	7.73×10^1	1.20×10^3	3.10×10^{-8}	3.03×10^{-8}	3.63×10^{-5}
M·1D_2O	2.08×10^1	1.49×10^2	1.53×10^{-8}	1.53×10^{-8}	2.28×10^{-6}
B·1H_2O	1.40×10^1	7.68×10^1	5.78×10^{-3}	5.41×10^{-3}	4.16×10^{-1}
B·1D_2O	8.07	4.20×10^1	2.27×10^{-3}	2.26×10^{-3}	9.49×10^{-2}
M·2H_2O	4.58	1.43×10^1	5.37×10^1	4.89×10^1	7.00×10^2
M·2D_2O	3.13	6.22	7.29	7.21	4.48×10^1
B·2H_2O	2.37	4.73	5.44×10^5	4.71×10^5	2.23×10^6
B·2D_2O	1.92	3.29	1.48×10^5	1.47×10^5	4.83×10^5

TABLE 4: Variational (η_{var}), Vibrational ($\eta^{\ddagger}_{vib}$), Tunneling (η_{tun}), and Total (η_t) Kinetic Isotope Effects at Different Temperatures for the 1,2-H Shift of Methoxyl and Benzyloxyl Radicals with One and Two Water Molecules

T (K)	η_{var}	$\eta^{\ddagger}_{vib}$	η_{tun}	η_t	η_{var}	$\eta^{\ddagger}_{vib}$	η_{tun}	η_t
	Methoxyl·1H_2O				Benzyloxyl·1H_2O			
200	0.96	2.83	27.89	75.86	0.92	3.30	3.39	10.34
250	0.97	2.33	15.87	35.87	0.93	2.85	2.42	6.39
300	0.97	2.04	8.04	15.92	0.94	2.55	1.83	4.28
400	0.98	1.68	2.52	4.16	0.96	2.18	1.30	2.73
500	0.98	1.48	1.59	2.31	0.97	1.95	1.15	2.18
	Methoxyl·2H_2O				Benzyloxyl·2H_2O			
200	0.88	14.82	4.38	57.12	0.81	5.48	1.93	8.59
250	0.90	9.82	3.13	27.67	0.84	4.36	1.62	5.94
300	0.92	7.38	2.30	15.62	0.87	3.69	1.44	4.61
400	0.94	5.07	1.59	7.58	0.93	2.87	1.25	3.32
500	0.95	3.95	1.33	4.99	0.94	2.47	1.16	2.69

suggest that the methoxyl radical does not rearrange in the EPR time scale ($k \geq 5 \times 10^5$ s^{-1}) at room temperature. The EPR experiments of Elford and Roberts,[11] showed that the ethoxyl radical did not rearrange either. However, rearrangement of the propyloxyl radical in water solvent was observed by Gilbert et al. at room temperature[10] with an estimated[7] pseudo-first-order rate constant of about 5×10^6 s^{-1}. The results of Konya et al.[7] imply that the pseudo-first-order rate constant for the 1,2-H shift of benzyloxyl radical in dry acetonitrile catalyzed by water is about 40 times larger than that for rearrangement of the propyloxyl radical in water. They attributed the faster rearrangement of the benzyloxyl radical compared with the propyloxyl radical to the benzylic stabilization of the produced ketyl radical. Our value for the 1:2 benzyloxyl complex is about 2 orders of magnitude slower. It should be also noticed that those experimental values are based on extrapolation of rate constants measured in acetonitrile containing relatively low concentrations of water and that our gas-phase model calculations cannot simulate the structure of the solvent. However, more important than the absolute value of the rate constants is to elucidate the mechanism of the 1,2-H shift. The measurements of Konya et al. of the 1,2-H shift of benzyloxyl radical in dried acetonitrile and benzene using 2-propanol as catalyst show that the plots of k_{exp} vs concentration of catalyst are straight lines. The experiments with water as catalyst gave similar results, indicating that the reaction is catalyzed by just one alcohol (or water) molecule. However, our calculations clearly indicate that the rearrangement involves the participation of two water molecules. It may be argued that acetonitrile may play a role in the rearrangement, which is not incorporated in our calculation, but their experimental measurements in benzene produced similar results, and it is difficult to see how this solvent may participate in the reaction. A possible interpretation is that the process with two water molecules may remain "kinetically invisible" if there is a preequilibrium between the radical and one water molecule, which is strongly displaced toward the formation of the complex. The rate-determining step for this process would be the evolution of the complex, after the incorporation of the second water molecule, toward the ketyl radical plus the two water molecules, i.e.

$$H_2O + PhCH_2O \rightleftarrows [(H_2O)(PhCH2O)] \qquad (7)$$

$$[(H_2O)(PhCH_2O)] + H_2O \xrightarrow{\text{slow}} PhCHOH + 2H_2O \qquad (8)$$

This mechanism was also discussed by Konya et al., but it was ruled out by them on the basis that at low concentrations of water the water molecules would be hydrogen-bonded to the acetonitrile instead of the radical. However, we think that this argument is difficult to sustain when the solvent is benzene.

The KIEs calculated for both radicals with one and two water molecules in the range of temperatures 200−500 K are listed in Table 4, and the logarithm of those values is plotted in Figure 5. The largest KIEs correspond to the rearrangement of the methoxyl radical. Specifically, at $T = 200$ K, the largest KIE corresponds to the 1:1 methoxyl−water complex, whereas at $T = 500$ K, it corresponds to the 1:2 complex. This trend is also observed for the water complexes with the benzyloxyl radical and the KIEs for the 1:1 and 1:2 complexes cross close to room temperature. At low temperatures, the main contribution to the KIE of the 1:1 complexes is due to tunneling (see Table 4), whereas for the 1:2 complexes, the main contribution is due to vibration. This is expected because for the 1:1 complexes only two hydrogens are moving and therefore the ratio H/D is smaller than for the 1:2 complexes, which involve the motion of three particles at the same time. On the other hand, the vibrational contribution to the KIE works in the opposite direction because the breaking of more bonds at the transition state involves an increase of this ratio. The KIE lines for the 1:1 and 1:2 complexes shown in Figure 5 cross because the KIE due to tunneling decreases faster than the KIE due to vibration. This difference in slope could be used as a probe whether the reaction is assisted by one or by two water (or alcohol) molecules.

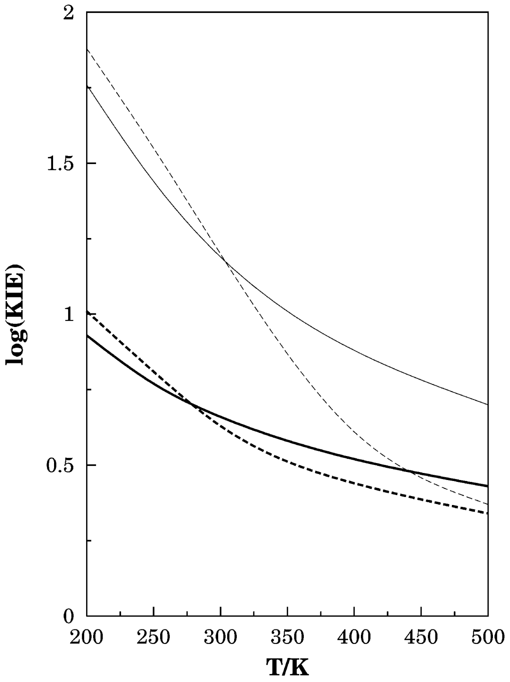

Figure 5. Plot of the logarithm of the total KIE vs temperature for the 1:1 complexes (thin-dashed line for methoxyl radical and thick-dashed line for benzyloxyl radical) and for the 1:2 complexes (thin-continuous line for methoxyl radical and thick-continuous line for benzyloxyl radical).

It should be noted that the vibrational contribution to the KIE for the 1:2 complexes with the methoxyl radical is larger than for the benzyloxyl radical. This is a consequence of a more synchronous transfer in the case of the methoxyl radical, because in the benzyloxyl radical the H_O hydrogen atom remains closer to the water molecule (O_2H_O distance of 1.068 Å in the benzyloxyl complex vs 1.136 Å in the methoxyl complex). In general, as shown by us elsewhere,[21,22] in a system for which the initial and final configurations are almost isoenergetic (like in the methoxyl−water complexes), the transfer is synchronous with high barrier heights and important contributions to KIE from tunneling and vibration. On the other hand, if the reaction is highly asymmetric (like in the benzyloxyl−water complexes), the transfer is more asynchronous with lower barrier heights and smaller contributions to KIE from tunneling and vibration. The contribution to the KIE because of rotation is not listed in Table 4 because its value is unity for all of the complexes studied here at all temperatures. The variational contribution lowers the KIE, although its value is not substantial because the MEP is quite sharp and the generalized transition state that minimizes the rate (the canonical variational transition state) is close to the saddle point.

Unfortunately, there are no measurements of the rate of the 1,2-H shift in benzene assisted by deuterated alcohols for the benzyloxyl rearrangement. The closest experiments related to our study were carried out by Elford and Roberts, who measured KIEs by deuterium incorporation unto the allylketyl radical product of the allyloxyl radical rearrangement using EtOD in cyclopropane at 220 K. They found that [1-deuterioxylallyl]/[1-hydroxylallyl] ratio depended on [EtOD], increasing almost linearly until [EtOD] = 0.6 M. This ratio then remains almost constant from 0.6 to 1.8 M [EtOD] and finally decreased at higher concentrations of EtOD. From the point of view of the mechanism through a two water molecules bridge proposed here, all of the ketyl radicals would be deuterated, which is the trend at low catalyst concentrations. However, our model cannot explain the decrease of the KIE at high catalyst concentrations. Elford and Roberts pointed out that a possible mechanism that incorporates hydrogen to the ketyl radical would be a direct 1,2-H shift from the carbon atom to the oxygen atom. However, the values of the barrier heights for this uncatalyzed process (see Table 2) indicate that this alternative mechanism can be ruled out. Another possibility, pointed out by Konya et al., is that EtOD under those experimental conditions tends to self-associate by forming dimers and oligomers, which may lead to reaction mechanism that may not occur with monomeric EtOD at room temperature.

5. Conclusions

In this paper, we presented a theoretical study of the rate constants and kinetic isotope effects of the 1,2-H shift of methoxyl and benzyloxyl radical in the presence of water molecules. We found out that the rearrangement reaction is catalyzed by water. Specifically, two water molecules participate in the reaction by forming a bridge that facilitates the hydrogen transfer. The rate constant for the rearrangement from the alkoxyl to ketyl form at room temperature for the methoxyl radical is calculated to be quite slow (7×10^2 s^{-1}), whereas the rate constant for the rearrangement of the benzyloxyl radical is around 2×10^6 s^{-1}. These values are in qualitative agreement with the experimental findings. We suggest a mechanism based on the initial formation of a 1:1 complex with the rate-determining step being the reaction after the incorporation of a second water molecule. The KIEs calculated in this paper are quite large because of important tunneling and vibrational contributions. This mechanism involves the complete deuteration of the ketyl radical which agrees qualitatively with the experimental observation at low concentrations of catalyst, although it cannot explain why the proportion of deuterated vs undeuterated ketyl radical decreases at large catalyst concentration.

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