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The Isomerization of Methoxy Radical: Intramolecular Hydrogen Atom Transfer Mediated through Acid Catalysis

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Supporting Information

ABSTRACT: The catalytic ability of water, formic acid, and sulfuric acid to facilitate the isomerization of the CH_3O radical to CH_2OH has been studied. It is shown that the activation energies for isomerization are 30.2, 25.7, 4.2, and 2.3 kcal mol^{-1}, respectively, when the reaction is carried out in isolation and with water, formic acid, or sulfuric acid as a catalyst. The formation of a doubly hydrogen bonded transition state is central to lowering the activation energy and facilitating the intramolecular hydrogen atom transfer that is required for isomerization. The changes in the rate constant for the CH_3O-to-CH_2OH isomerization with acid catalysis have also been calculated at 298 K. The largest enhancement in the rate, by over 12 orders of magnitude, is with sulfuric acid. The results of the present study demonstrate the feasibility of acid catalysis of a gas-phase radical isomerization reaction that would otherwise be forbidden.

Because of differences in bonding, structural isomers can exhibit large variations in their reactivities. Hence, exploring mechanisms that have the potential to readily interconvert one isomer into another is critical for assessing the overall reactivity of an isomeric system. In this work, we examined the ability of a single acidic solvent molecule to catalyze the interconversion between the methoxy (CH_3O) and hydroxymethyl (CH_2OH) radicals by forming a doubly hydrogen bonded transition state, which facilitates intramolecular hydrogen atom transfer.

The methoxy radical plays an important role in both combustion and atmospheric chemistry; as a result, its kinetics, spectroscopy, and dynamics have received a great deal of attention.[1−4] In the atmosphere, CH_3O is formed primarily through the oxidation of CH_4 via the following mechanism:[5]

$$CH_4 + OH \rightarrow CH_3 + H_2O \tag{1}$$

$$CH_3 + O_2 + M \rightarrow CH_3O_2 + M \tag{2}$$

$$CH_3O_2 + NO \rightarrow CH_3O + NO_2 \tag{3}$$

Upon its formation, the fate of CH_3O is dictated by competition between several loss processes, including isomerization (eq 4), unimolecular dissociation (eq 5), and bimolecular reaction (eq 6):

$$CH_3O \rightarrow CH_2OH \tag{4}$$

$$CH_3O \rightarrow CH_2O + H \tag{5}$$

$$CH_3O + O_2 \rightarrow CH_2O + HO_2 \tag{6}$$

As the barriers for unimolecular dissociation and isomerization are quite high (24−35 and 26−36 kcal mol^{-1}, respectively),[3,4,6−11] under atmospheric conditions, the primary loss mechanism for CH_3O is its bimolecular reaction with molecular oxygen to form formaldehyde and hydroperoxy radical.[12]

The recommended rate constant for reaction 6 at 298 K is 1.9×10^{-15} cm^3 $molecule^{-1}$ s^{-1}.[13,14] In contrast to the rather slow reactivity of CH_3O with O_2, the hydroxymethyl radical (CH_2OH) reacts rapidly with O_2, having a rate constant of 9.1×10^{-12} cm^3 $molecule^{-1}$ s^{-1} at 298 K.[14] The large difference in the rates for the $CH_3O + O_2$ and $CH_2OH + O_2$ reactions led Radford in 1980 to state that "this has importance for atmospheric chemistry, for if isomeric rearrangement of CH_3O to CH_2OH can occur even to a small extent, then the oxidation of CH_3O in the upper atmosphere maybe governed by unimolecular isomerization rather than by bimolecular reaction."[15] It is now well-established that the high barrier for isomerization makes the direct interconversion between isolated CH_3O and CH_2OH improbable; the viability for this barrier to be significantly reduced through a catalytic reaction with water or other relevant atmospheric species has not been hitherto explored. Specifically, in this study we illustrate the catalytic role that water, formic acid, and sulfuric acid can exhibit in facilitating the interconversion between CH_3O and CH_2OH in the gas phase (eq 7):

$$CH_3O + X\ [X = H_2O, HC(O)OH, H_2SO_4] \rightarrow CH_2OH + X \tag{7}$$

We note that although there have been several prior studies showing the ability of a single solvent molecule to greatly reduce the activation energy for various reactions,[16−20] this is the first investigation to explore the ability of acidic solvents to catalyze *free radical isomerization*. Our results give insight into a possible new gas-phase mechanism for the oxidation of hydrocarbons under humid and acidic conditions as well as the catalytic roles of acids in previously forbidden radical reactions.

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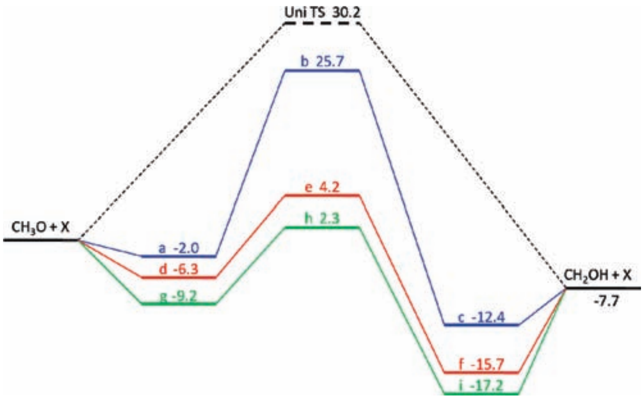

Figure 1. Variation in potential energy along the reaction coordinate for methoxy radical isomerization mediated by solvent X at the CCSD(T)/aug-cc-pVTZ//QCISD/6-31G(d) level including ZPE (energies in kcal mol): black dashed curve, no solvent; blue curve, water catalysis; red curve, formic acid catalysis; green curve, sulfuric acid catalysis.

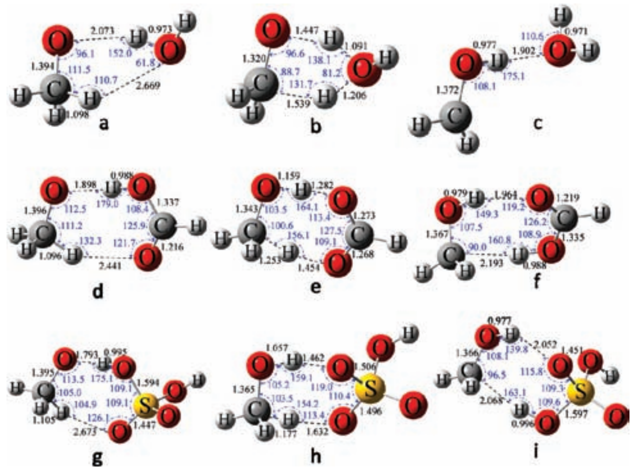

Figure 2. Structures of stationary points along the QCISD/6-31G(d) potential energy surfaces for the reactions catalyzed by (a−c) water, (d−f) formic acid, and (g−i) sulfuric acid (bond lengths in Å, angles in deg).

The isomerization of isolated methoxy radicals proceeds through a three-membered-ring-like transition state. At the CCSD(T)/aug-cc-pVTZ level of theory, the activation energy obtained in this study was 30.2 kcal mol^{-1} (Figure 1; also see Supplementary Table 1 in the Supporting Information), in good agreement with results of prior studies, which range between 26.1 and 36.0 kcal mol^{-1}.[6−10] In particular, the most recent calculations of Tachikawa et al.[10] reported an energy barrier of 32.88 kcal mol^{-1} at the CCDST4/D95 V** level of theory.

The introduction of water as a collision partner results in the potential energy curve represented by the blue line in Figure 1. The potential exhibits a five-membered-ring prereactive complex arising from hydrogen bonding between the methoxy and water molecules. This complex, shown in Figure 2a, has a binding energy of 2.0 kcal mol^{-1}. In the transition state for the reaction with water (Figure 2b), water acts as a bridge for hydrogen atom transport, with the oxygen on water abstracting the hydrogen atom from the methoxy radical as the methoxy radical in turn abstracts a hydrogen atom from water. The inclusion of a single water molecule reduces the activation energy by over 4 kcal mol^{-1} to 25.7 kcal mol^{-1} (Figure 1). With formic acid acting as the catalyst, the reaction potential energy (represented by the red curve in Figure 1) also displays prereactive and postreactive complexes (Figure 2d,f) analogous to those found with water. However, formic acid forms substantially stronger hydrogen bonds with the radicals, and this is reflected in the increased binding energies for these complexes, which are 6.3 kcal mol^{-1} and 15.7 kcal mol^{-1} with respect to the reactants (Figure 1d,f). In going from a five-membered-ring transition state in the case of water to the seven-membered ring for formic acid, the steric strain is eased. This in turn reduces the activation energy for isomerization in the case of formic acid to 4.2 kcal mol^{-1}, which amounts to a decrease of 26.0 kcal mol^{-1} relative to that for the isolated unimolecular reaction. An inspection of the seven-membered-ring transition-state structure associated with the formic acid reaction (Figure 2e) reveals that formic acid forms a doubly hydrogen bonded complex with the CH_3O radical. The hydrogen atom transfer required for isomerization is facilitated by abstraction of the hydrogen on the methoxy radical by the carbonyl oxygen atom on formic acid, while the oxygen on methoxy radical in turn abstracts the acidic hydrogen on formic acid. Introducing sulfuric acid as the catalyst reveals a trend that is similar to the two previous cases. The reaction potential energy (shown in green in Figure 1) exhibits a prereactive complex (Figure 2g) with a strong hydrogen bond having a binding energy of 9.2 kcal mol^{-1}. The transition state (Figure 2h) is similar to the one for formic acid, with the sulfuric acid now aiding in the migration of the hydrogen atom. Sulfuric acid reduces the isomerization barrier by 27.9 kcal mol^{-1} to 2.3 kcal mol^{-1}, and the reaction proceeds to products via a postreactive complex (Figure 2i) with two hydrogen bonds between CH_2OH and H_2SO_4 and a binding energy of 17.2 kcal mol^{-1} with respect to the reactants. Thus, for both of the acids, the formation of a seven-membered-ring-like transition state involving two hydrogen bonds between the radical and the acid solvent leads to a significant decrease in the activation energy for isomerization. The rate constants calculated at 298 K for the CH_3O radical isomerization as catalyzed by water, formic acid, and sulfuric acid are presented in Supplementary Table 2. As expected, the rate constant for water is quite small, if not negligible (1.23×10^{-26} cm^3 $molecule^{-1}$ s^{-1}), making this reaction insignificant for the removal of CH_3O. There is an enhancement in the rate constant to 4.19×10^{-16} cm^3 $molecule^{-1}$ s^{-1} when formic acid is used as the catalyst. However, the most significant rate enhancement is with sulfuric acid, for which the rate constant is 9.12×10^{-14} cm^3 $molecule^{-1}$ s^{-1}. Hence, there is an enhancement of over 12 orders of magnitude in going from water to sulfuric acid as the catalyst. In fact, these data suggest that the gas-phase isomerization of CH_3O to CH_2OH, which in isolation is not possible, becomes plausible in the presence of sulfuric acid; the reaction is still slow but no longer negligible. Additional rate estimates from an RRKM analysis also affirm these results (see the Supporting Information for details).

In summary, a potential catalytic pathway for the isomerization of CH_3O radical via reaction with water, formic acid, or sulfuric acid has been investigated. In each of these three cases, the transition state for reaction entails the formation of a doubly hydrogen bonded species involving the radical and the solvent molecule, which in turn facilitates hydrogen atom transfer and results in a large decrease in barrier height. The reduction for formic acid and sulfuric acid are 21.3 and 23.4 kcal mol^{-1} respectively, resulting in corresponding increases in the isomerization rate by roughly 10 and 12 orders of magnitude, respectively, relative to that for water. The present results suggest that acid catalysis not only should be an important mechanism for lowering the activation energy of the methoxy radical isomerization but by extension is also likely to be a significant pathway for the isomerization of other radicals that involve intramolecular hydrogen atom transfer.[21]

ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Details of the methods used and tables of relative energies, rate constants (TST and RRKM), total energies, frequencies, and geometries. This material is available free of charge via the Internet at http://pubs.acs.org.

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