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Inorganic acid-catalyzed tautomerization of vinyl alcohol to acetaldehyde

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ABSTRACT

The vinyl alcohol–acetaldehyde tautomerization reaction has recently received considerable attention as a potential route for the formation of organic acids in the troposphere (Andrews et al., 2012 [7]). We examine the catalytic effect of inorganic acids in the troposphere (e.g. HNO_3, H_2SO_4 and $HClO_4$) on the vinyl alcohol–acetaldehyde tautomerization reaction, by means high-level thermochemical procedures. We show that H_2SO_4 and $HClO_4$ catalysts lead to near-zero reaction barrier heights for the vinyl alcohol → acetaldehyde reaction, and to low reaction barrier heights in the reverse direction ($\Delta H^{\ddagger}_{298} = 40.6$ and 39.5 kJ mol^{-1}, respectively).

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1. Introduction

Small carboxylic acids are the most abundant organic acids in the troposphere and play a key role in acid deposition [1–5]. Despite their abundance, current kinetic models are not able to accurately predict their formation in both the urban and rural troposphere, implying a missing secondary source for carboxylic acids [1]. Shallcross and co-workers, showed that oxidation of vinyl alcohol significantly enhances the formation of formic acid in the troposphere, and suggest that enolic species may be the missing secondary source of carboxylic acids [2]. Recently, Jordan, Kable and co-workers proposed that photo-induced tautomerization of acetaldehyde to vinyl alcohol is a potential route for the formation of vinyl alcohol in the troposphere [6–8].

The uncatalyzed keto-enol tautomerization reaction has a high barrier and is not a viable route under tropospheric conditions ($\Delta H^{\ddagger}_{298} = 236.1$ kJ mol^{-1}, relative to the free vinyl alcohol, *vide infra*) [7,9,10]. In the present Letter, we examine the catalytic effect of species that are of atmospheric importance on the vinyl alcohol ↔ acetaldehyde tautomerization reaction. High-level ab initio calculations (with the W1–F12 thermochemical protocol) [11] were performed in the gas-phase in order to explore the uncatalyzed and catalyzed potential energy surfaces (Section 2). We consider the following catalysts: sulfuric acid (H_2SO_4), perchloric acid ($HClO_4$), phosphoric acid (H_3PO_4), carbonic acid (H_2CO_3), formic acid ($HC(O)OH$), nitric acid (HNO_3), hydroperoxyl radical (HO_2) and water (H_2O). We show that a double proton shift between the catalyst and the substrate can lead to energetically low-lying transition structures (TSs) for the gas-phase tautomerization reaction. In particular, the H_2SO_4 and $HClO_4$ catalysts lead to submerged barrier heights on the enthalpic surface at 298 K ($\Delta H^{\ddagger}_{298}$)

(relative to the free vinyl alcohol), and to low reaction barrier heights of 40.6 and 39.5 kJ mol^{-1}, respectively (relative to the free acetaldehyde). These findings may have significant consequences for current atmospheric chemical models since mineral acids (e.g. H_2SO_4 and HNO_3) and the hydroperoxy radical are prominent species in the troposphere [3,12–16].

2. Computational methods

High-level ab initio calculations were performed in order to explore the potential energy surface for the uncatalyzed and catalyzed tautomerization reaction. The W1 thermochemical protocol [17] (and its explicitly-correlated W1–F12 version) [11] are widely used for the calculation of thermochemical and kinetic properties [18,19]. These theories represent a layered extrapolation to the relativistic, all-electron CCSD(T) (coupled cluster with singles, doubles, and quasiperturbative triple excitations) basis-set-limit energy, and can achieve 'sub-chemical accuracy' (e.g., they are associated with a mean absolute deviation from accurate atomization energies of 2.0 kJ mol^{-1}) for molecules whose wave functions are dominated by dynamical correlation [11,17–23].

The geometries of all structures have been obtained at the B3LYP-D3/A′VTZ level of theory [24,25], where A′VnZ indicates the combination of the standard correlation-consistent cc-pVnZ basis sets on H [26], the aug-cc-pVnZ basis sets on first-row elements [27], and the aug-cc-pV(n+d)Z basis sets on second-row elements [28]. Harmonic vibrational analyses have been performed to confirm each stationary point as either an equilibrium structure (i.e., all real frequencies) or a transition structure (TS) (i.e., with one imaginary frequency). Zero-point vibrational energy (ZPVE) and enthalpic corrections have been obtained from such calculations. The connectivities of the transition structures were confirmed by performing intrinsic reaction coordinate (IRC)

calculations [29]. All geometry optimizations and frequency calculations were performed using the GAUSSIAN 09 program suite [30].

In order to obtain reliable reaction energies and barrier heights for the uncatalyzed and catalyzed reactions, calculations have been carried out using the high-level, ab initio W1–F12 and W1 procedures with the MOLPRO 2012.1 program suite [31]. W1–F12 combines explicitly-correlated F12 methods [32,33] with extrapolation techniques in order to approximate the CCSD(T) basis-set-limit energy. Due to the drastically accelerated basis-set convergence of the F12 methods [34,35], W1–F12 is superior to the original W1 method not only in terms of performance but also in terms of computational cost [11]. The computational protocol of the W1–F12 method has been specified and rationalized in detail in Ref. [11]. In brief, the Hartree–Fock component is extrapolated from the VDZ-F12 and VTZ-F12 basis sets, using the $E(L) = E_\infty + A/L^\alpha$ two-point extrapolation formula, with $\alpha = 5$ (where VnZ-F12 denotes the cc-pVnZ-F12 basis sets of Peterson et al. [34] which were specifically developed for explicitly correlated calculations). The valence CCSD-F12 correlation energy is extrapolated from the same basis sets, using the same two-point extrapolation formula but with $\alpha = 3.67$. In all of the explicitly-correlated coupled cluster calculations the diagonal, fixed-amplitude 3C(FIX) ansatz [36,37] and the CCSD-F12b approximation are employed [38]. The (T) valence correlation energy is obtained in the same way as in the original W1 theory [17], i.e., extrapolated from the A′VDZ and A′VTZ basis sets using the above two-point extrapolation formula with $\alpha = 3.22$. The CCSD inner-shell contribution is calculated with the core-valence weighted correlation-consistent aug′-cc-pwCVTZ basis set of Peterson and Dunning [39], whilst the (T) inner-shell contribution is calculated with the cc-pwCVTZ(no f) basis set (where cc-pwCVTZ(no f) indicates the cc-pwCVTZ basis set without the f functions). The scalar relativistic contribution (in the second-order Douglas–Kroll–Hess approximation) [40,41] is obtained as the difference between non-relativistic CCSD(T)/A′VDZ and relativistic CCSD(T)/A′VDZ-DK calculations [42]. The diagonal Born–Oppenheimer corrections (DBOC) are calculated at the HF/A′VTZ level of theory.

3. Results and discussion

It is well known that the presence of one (or more) water molecules can significantly enhance the reaction rates of prototropic tautomerizations in the gas phase relative to the rates of the uncatalyzed reactions [9,12,43–45]. For the vinyl alcohol → acetaldehyde tautomerization reaction one water catalyst reduces the barrier by more than 50%. Specifically, at the W1–F12 level, the following barriers ($\Delta H_{298}^\ddagger$) are obtained: 236.1 (uncatalyzed) and 104.4 (H_2O catalyst) kJ mol^{-1}. Figure 1a and b shows the TSs for the uncatalyzed and catalyzed reactions. In part, the barrier reductions may be attributed to the reduced strain energy in the TSs, as the addition of a water molecule allows for the formation of a six-membered-ring TS compared with the four-membered-ring TS in the uncatalyzed reaction [44,45].

Recently, da Silva found that a formic acid catalyst (HC(O)OH) significantly enhances the rate of the vinyl alcohol ↔ acetaldehyde tautomerization reaction [9]. He also pointed out that other catalysts in which a carbonyl oxygen and a hydroxyl group are bound to a common atom are expected to posses catalytic properties. Using the composite G3SX procedure [46,47], he calculated an enthalpic barrier ($\Delta H_{298}^\ddagger$) of 236.8 kJ mol^{-1} for the uncatalyzed tautomerization, and a barrier of 23.4 kJ mol^{-1} for the reaction catalyzed by a formic acid catalyst. Table 1 gives the W1–F12 enthalpies at 298 K (ΔH_{298}) for the reactant complexes (RC), transition structures (TS), and product complexes (PC) located along the catalyzed pathways for the vinyl alcohol → acetaldehyde
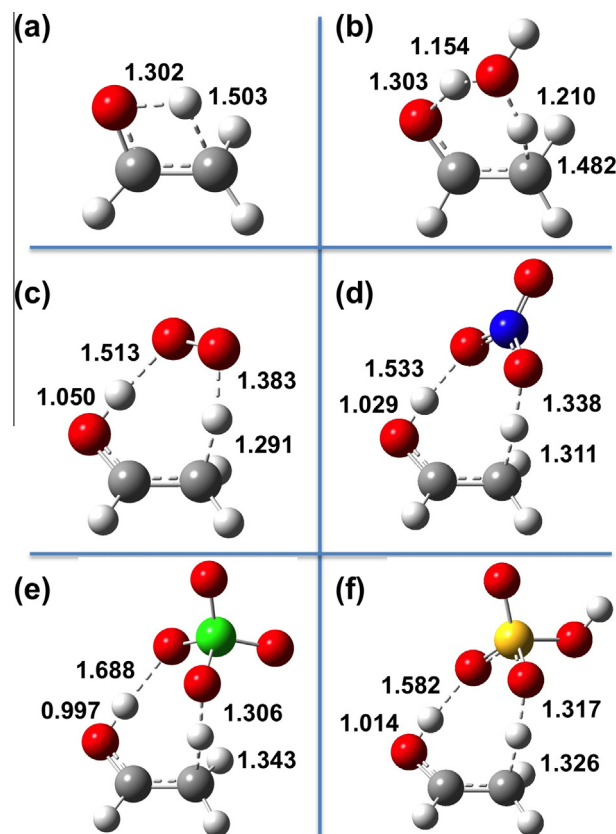

Figure 1. B3LYP-D3/A′VTZ optimized transition structures for the vinyl alcohol ↔ acetaldehyde tautomerization reaction: (a) uncatalyzed; and catalyzed by: (b) H_2O, (c) HO_2, (d) HNO_3, (e) $HClO_4$ and (f) H_2SO_4. The bonds being broken and formed in the transition structures are represented by single dashed lines, and the lengths of these bonds are given in Å. Atomic color scheme: H, white; C, gray; N, blue; O, red; S, yellow; Cl, green. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

reaction. A schematic representation of the enthalpy energy profile is given in Figure 2. For the uncatalyzed reaction we obtain a barrier of 236.1 kJ mol^{-1}, which is in excellent agreement with the reaction barrier of da Silva [9]. An HO_2 radical catalyst reduces the barrier by more than 80% ($\Delta H_{298}^\ddagger = 46.6$ kJ mol^{-1}). In part, HO_2 is a more effective catalyst than H_2O due to the reduced strain energy associated with a seven-membered-ring TS (HO_2 catalyst, Figure 1c) relative to a six-membered-ring TS (H_2O catalyst, Figure 1b). This is demonstrated by angles between the O—C—C backbone of the substrate and the protons that are being transferred. Specifically, the ∠C—C···H angles are 66.8° (uncatalyzed TS, Figure 1a), 91.8° (H_2O catalyst, Figure 1b) and 102.8° (HO_2 catalyst, Figure 1c), and the C—O···H angles are 76.9° (uncatalyzed TS), 102.5° (H_2O catalyst) and 108.5° (HO_2 catalyst). A formic acid catalyst results in a W1–F12 reaction barrier of 26.2 kJ mol^{-1}. We note that the G3SX barrier of da Silva [9] (23.4 kJ mol^{-1}) is in good agreement with our benchmark W1–F12 barrier, in accordance with the expected accuracy of the more approximate G3SX procedure for reaction barrier heights [11,44,45,48,49]. The reaction barrier obtained with the formic acid catalyst is lower by 20.4 kJ mol^{-1} than the one obtained with the HO_2 catalyst (Table 1). Again, this may be attributed in part to the reduction in strain energy when moving from a seven-membered-ring TS to an eight-membered-ring TS.

We turn now to the catalytic activity of the inorganic acids (HNO_3, H_2CO_3, H_3PO_4, $HClO_4$ and H_2SO_4). Figure 1d–f shows the TSs for the HNO_3, $HClO_4$ and H_2SO_4 catalysts, while the reaction barrier heights are given in Table 1 (and Figure 2). A common