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Keto–Enol Kinetics

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Carboxylic Acid Catalyzed Keto-Enol Tautomerizations in the Gas Phase**

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Carboxylic acids are the products of incomplete combustion and of the atmospheric oxidation of biogenic and anthropogenic volatile organic compounds (VOCs). As such, carboxylic acids are found at high levels throughout the troposphere (typically in the ppb range),[1] and are present in combustor exhaust gases. Carboxylic acids, as hydrogen bond donors and acceptors, can form relatively strong complexes with organic molecules in the gas phase; this is particularly true for organic substrates functionalized with carbonyl, alcohol, and other heteroatomic groups. There is a great deal of interest in the ability of hydrogen-bound complexes to influence the kinetics and the products of gas-phase reactions.[2,3] For example, it has been demonstrated that a water molecule bound to acetaldehyde (a complex with a bond dissociation energy of approximately 5 kcal mol^{-1}) increases the rate of hydrogen abstraction by the hydroxyl (OH) radical.[3] This finding is supported by theoretical calculations, which reveal that water facilitates, but does not directly participate in, the hydrogen-abstraction reaction.

Herein we demonstrate that carboxylic acids catalyze intramolecular hydrogen shifts in the gas phase, through the initial formation of a hydrogen bonded complex followed by a double-hydrogen-shift (DHS) reaction. The transfer of hydrogen atoms within and between molecules is ubiquitous in gas-phase reactions, and the generic DHS mechanism reported here has the potential to influence a wide range of reaction processes. This study uses quantum chemistry and statistical reaction rate theory techniques to calculate the rate constants for the formic acid catalyzed conversion of vinyl alcohol (ethenol) to acetaldehyde, that is, the simplest keto–enol tautomerization. Furthermore, we demonstrate that this process is competitive with photochemical oxidation of the enol. Enols, which are the less stable isomers of carbonyl compounds, have recently emerged as significant combustion intermediates,[4] and are implicated in the photochemical oxidation of isoprene.[5]

Quantum chemical calculations are performed at the composite G3SX level of theory.[6] This theoretical method uses B3LYP/6-31G(2df,p) structures and vibrational frequencies, with a series of higher-level wavefunction theory energy calculations, up to QCISD(T) theory, performed on the B3LYP structures. The G3SX method is broadly accurate for thermochemistry and kinetics, and both the reaction energies and the barrier heights reported here are expected to have an average uncertainty of below 1 kcal mol^{-1}.[6,7] Rate constants for the barrierless association of vinyl alcohol and acetaldehyde with formic acid were determined by using variational transition state theory (VTST). The rate constants were calculated to be in the range 10^{-12}–10^{-11} cm^3 molecule^{-1} s^{-1}, and are relatively insensitive to the temperature (consistent with a barrierless process). The VTST calculations were performed on G3SX level potential energy profiles (see the Supporting Information for a detailed description of the calculations). The apparent rate constants in the chemically activated vinyl alcohol + formic acid → acetaldehyde + formic acid process (and in the slower reverse reaction) are determined as a function of temperature and pressure by solving the time-dependent master equation, with RRKM theory for microcanonical rate constants, $k(E)$. Initial calculations between 0.01–100 atm revealed these reactions to be insensitive to pressure, and all the reported values are calculated at 1 atm. For the double-hydrogen-shift step, tunneling corrections are applied using an Eckart barrier, approximated from the imaginary vibrational frequency of the transition state (1354.3 cm^{-1}) and the 0 K forward and reverse reaction barriers. Master equation calculations are performed with an energy grain of 0.1 kcal mol^{-1}, up to a maximum energy of 100 kcal mol^{-1}. Lennard-Jones parameters for the active $C_3H_6O_3$ isomers are 5.4 Å and 400 K, where energy transfer is treated using an exponential-down model with $\Delta E_{\mathrm{down}} = 1000$ cm^{-1}. Nitrogen was used as the bath gas. The rate constants calculated for the forward and reverse reaction processes are reported in the form $k = A' T^n \exp(-E_a/RT)$, where k and $A' T^n$ are in cm^3 molecule^{-1} s^{-1}, the activation energy E_a is in cal mol^{-1}, and the temperature T in K. All the electronic structure theory calculations are performed using Gaussian 03,[8] and the rate constant calculations are conducted with the software ChemRate 1.5.9.[9]

The transition-state structure for the formic acid catalyzed conversion of vinyl alcohol to acetaldehyde is shown in Figure 1 (with imaginary frequency displacement vectors). The corresponding enthalpy profile for this reaction is shown in Figure 2, where the uncatalyzed unimolecular reaction is also illustrated. Note that the use of carboxylic acids other than formic acid has a negligible effect on both the transition-state structure and on the reaction energetics. Figure 1 shows that the DHS process involves concerted movement of two hydrogen atoms, thus resulting in proton exchange between the reactants. However, the net effect is the transformation of

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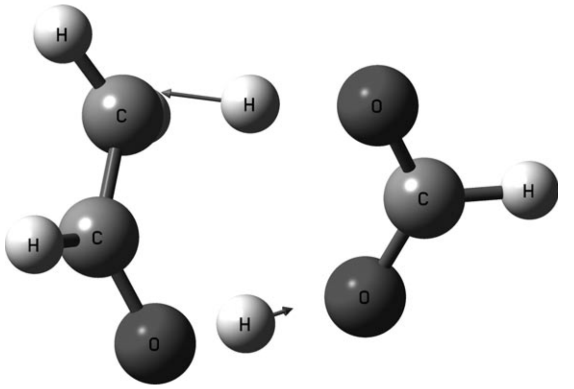


Figure 1. Double-hydrogen-shift (DHS) transition state in the reaction of vinyl alcohol with formic acid (B3LYP/6-31G(2df,p).

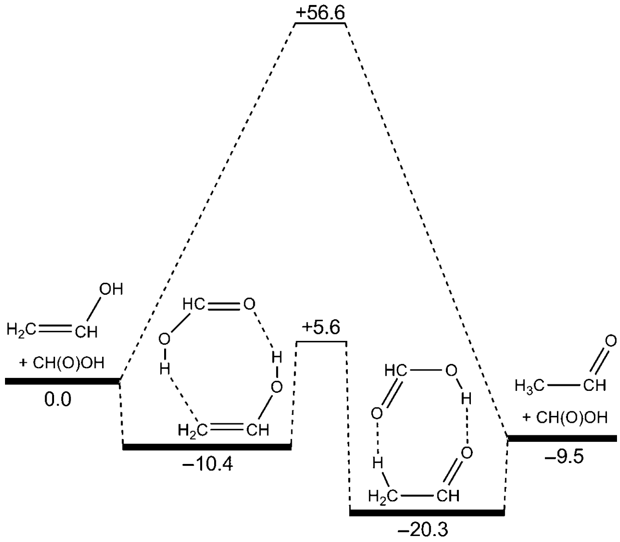


Figure 2. Enthalpy profile for the reaction of vinyl alcohol with formic acid (G3SX 298 K enthalpies, kcal mol^{-1}).

vinyl alcohol into acetaldehyde (or vice versa), thus leaving the carboxylic acid essentially unchanged. We can see from Figure 2 that this DHS mechanism reduces the barrier for the keto–enol tautomerization from 56.6 kcal mol^{-1} to only 5.6 kcal mol^{-1} (relative to the enol form). Such low-energy DHS reactions are thought to play a role in the unimolecular isomerization of some alkoxyl radicals,[10] but have not previously been shown to have such a drastic effect on a bimolecular reaction. The key feature of this mechanism is that the acid catalyst donates or accepts hydrogen atoms at different oxygen atom sites, which results in a degenerate isomerization process that allows for an unstrained transition state. The same process is well-known in carboxylic acid dimers, where it is responsible for proton tunneling,[11] which is an important biochemical phenomenon.[12]

The ability of carboxylic acids to facilitate intramolecular hydrogen atom transfers as described here is novel, but should not be unique, as there are a range of compounds with =O and OH groups bound to a common (or equivalent) atom. A similar mechanism to that expounded here can also occur where a hydrogen atom is donated and accepted from the same oxygen atom within a molecule, although in this case the transition state is considerably strained, while the participating oxygen atom has a three-coordinated bonding motif (demonstrated for vinyl alcohol + H_2O in the Supporting Information). As a result, the barrier is relatively large, with a modest catalytic effect.

Rate constants have been calculated for the chemically activated vinyl alcohol + formic acid, → acetaldehyde + formic acid reaction (as well as for the reverse process) from 300 to 2000 K at 1 atm, and are plotted in Figure 3. Although the reverse dissociation of the initially activated $[C_3H_6O_3]^*$ adduct is the major process in the reaction between vinyl alcohol and formic acid, branching to form the acetaldehyde/formic acid complex (which promptly dissociates) is also significant, and rate constants for this chemically activated process are still relatively large. The rate constants in the isomerization reaction between vinyl alcohol and formic acid are essentially independent of temperature, with a small negative activation energy at low temperatures (from the barrierless reaction) and a small positive activation energy at higher temperatures (resulting from the 5.6 kcal mol^{-1} reaction barrier). In the reaction between acetaldehyde and formic acid, the rate constants calculated for the isomerization to vinyl alcohol consistently increase with increasing temperature, owing to the larger overall barrier. The chemically activated vinyl alcohol + formic acid→acetaldehyde + formic acid reaction is described by the rate constant expression $k = 4.67\times10^{-26}T^{3.286}\exp(+4509/RT)$ cm^3 molecule^{-1} s^{-1}, with $k = 1.17\times10^{-19}T^{1.209}\exp(-556/RT)$ cm^3 molecule^{-1} s^{-1} for the reverse reaction.

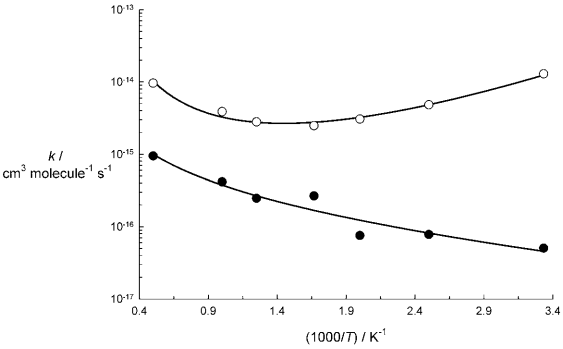
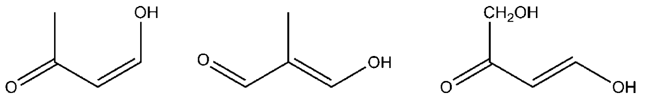


Figure 3. Calculated rate constants for the formic acid catalyzed conversion of vinyl alcohol to acetaldehyde, and vice versa. Filled circles: $CH_3CHO \rightarrow CH_2CHOH$; empty circles: $CH_2CHO \rightarrow CH_3CHO$.

At 300 K, the formic acid catalyzed keto–enol tautomerization of vinyl alcohol proceeds at 1.30×10^{-14} cm^3 molecule^{-1} s^{-1}. Given a typical tropospheric formic acid concentration of 1 ppb,[1] this results in a vinyl alcohol lifetime of only 52 min. Considering the range of total carboxylic acid concentrations encountered throughout the troposphere, the predicted lifetime of vinyl alcohol could vary from tens of minutes to hours. This process is expected to compete predominantly with the destruction of the enol initiated by the OH radical (itself a carboxylic acid source),[13] where the lifetime of the vinyl alcohol is estimated to be on the order of 5 to 46 h (given [OH] of 10^6–10^7 molecule cm^{-3} and $k = 6\times10^{-12}$ cm^3 molecule^{-1} s^{-1}).[13] Thus, it appears that the carboxylic acid catalyzed keto–enol tautomerization can compete with the OH-initiated oxidation in the atmosphere. The significance of this new chemistry to combustion is less clear, although it could be of particular importance with regard to exhaust gases, where acid concentrations on the order of hundreds of ppt and above would reduce the enol lifetime to tens of seconds and below.

This work demonstrates that carboxylic acids can catalyze gas-phase keto–enol tautomerizations on timescales that are relevant to atmospheric and combustion chemistry. Enols are thought to occur as intermediates in a number of reacting gas-phase systems,[4,5] yet are often not included in kinetic models because of an incomplete knowledge of their chemistry. The enols shown in Scheme 1 are suggested as intermediates in the isoprene photooxidation mechanism, with keto–enol tautomerization through an unknown heterogeneous process invoked to describe their rapid conversion into the observed aldehyde forms.[5] The implicit inclusion of enols such as these in VOC oxidation mechanisms, with gas-phase keto–enol tautomerization in competition with OH-initiated enol destruction, could provide a large new carboxylic acid source.[13] Similarly, keto–enol tautomerization is an important step in the coupling of chlorinated phenoxyl radicals,[14] which contributes to the formation of toxic polychlorinated dibenzodioxins (PCDDs) in incinerators. Current gas-phase models fail to describe observed PCDD levels,[15] and once again poorly understood heterogeneous chemistry is often implicated.



Scheme 1. Enols suggested as intermediates in the photooxidation of isoprene.[5]

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