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The Gas Phase Aldose-Ketone Isomerization Mechanism: Direct Interconversion of the Model Hydroxycarbonyls 2-Hydroxypropanal and Hydroxyacetone

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ABSTRACT

We report a novel mechanism for the interconversion of 2-hydroxypropanal with its more-stable ketone isomer hydroxyacetone. Reaction proceeds via concerted transfer of two H atoms, requires a barrier of only ~40 kcal mol^{-1}, bypasses the enediol intermediate, and is general for α-hydroxy carbonyls. A similar isomerization mechanism is shown to persist for β, γ, and δ-hydroxy carbonyls; these compounds are skeletal forms of the monosaccharides and this work therefore discloses the gas-phase mechanism for aldose-ketose isomerization. As an example, the isomerization of glyceraldehyde to dihydroxyacetone is shown to proceed via this mechanism with a barrier of 31 kcal mol^{-1}. Rate coefficients and thermochemical properties are reported for the isomerization of 2-hydroxypropanal and hydroxyacetone for use in detailed kinetic models. Additionally, RRKM theory $k(E)$ values for this reaction suggest that it may transpire in the troposphere following solar excitation.

Hydroxycarbonyls are common oxygenated intermediates formed in the photochemical oxidation of volatile organic compounds and in the thermal processing of lignocellulosic material. Hydroxyacetone ($HOCH_2C(O)CH_3$), the simplest α-hydroxy ketone, is a widely-detected trace gas in the troposphere,[1] and its photochemical oxidation mechanisms have been studied extensively.[2-5] 2-Hydroxypropanal ($CH_3CHOHCHO$), an isomer of hydroxyacetone, is an intermediate in the pyrolysis and combustion chemistry of glyceral.[6] More broadly, the open-chain forms of the monosaccharides are hydroxycarbonyls, with an aldehyde (aldose) or ketone (ketose) moiety and a hydroxyl group at each remaining carbon. Hydroyxacetone and 2-hydroxypropanal thus serve as model compounds for the α-hydroxy carbonyl functionality in these simple sugars.

Recently, we reported on the isomerization mechanism of glycolaldehyde ($HOCH_2CHO$),[7] the archetypal α-hydroxy carbonyl and an important tropospheric compound in its own right.[8] This work revealed that glycolaldehyde could undergo keto-enol tautomerization via intramolecular transfer of two H atoms, mediated by the hydroxyl group. This process is reminiscent of a bimolecular mechanism previously shown to catalyze keto-enol tautomerizations.[9] In the course of our investigation into glycolaldehyde it became apparent that this compound could undergo degenerate isomerization reactions in which the unique O atoms (*i.e.*, the alcohol and aldehyde functional groups) were effectively scrambled. The present work extends this analysis to hydroxycarbonyl compounds in which the alcohol and aldehyde/ketone groups are not interchangeable, starting with the hydroxyacetone/2-hydroxypropanal pairing, through the application of *ab initio* calculations and reaction rate theory modelling. This study expands our understanding of rearrangement reactions available to hydroxycarbonyl compounds in thermal environments and in the troposphere. Moreover, it sheds light on aldose-ketose isomerizations, which are involved in the thermal and chemical processing of carbohydrates[10-13] and are also biochemically important.[14,15]

A reaction mechanism for isomerization of hydroxyacetone and 2-hydroxypropanal is shown in Figure 1. Included in this mechanism are low-energy pathways for the decomposition of these compounds, including a unimolecular pathway in 2-hydroxypropanal that leads to vinyl alcohol via the elimination of formaldehyde. Figure S1 of the Supporting Information illustrates the complete set of bond dissociation energies in hydroxyacetone and 2-hydroxypropanal. The $C_3O_2H_6$ isomers involved in Figure 1 are shown in Figure S2, with the transition state structures included as Figure S3.

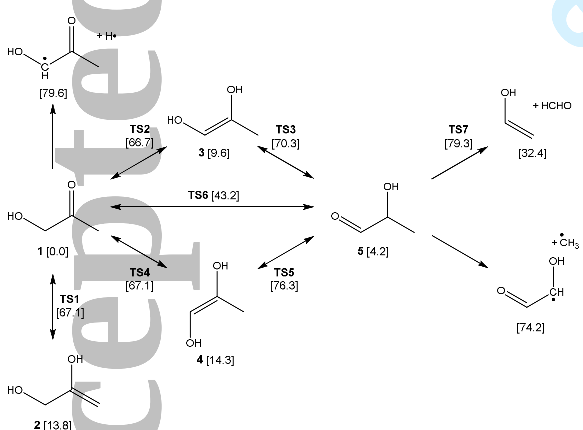

Figure 1. Reaction mechanism for isomerization of hydroxyacetone [**1**] and 2-hydroxypropanal [**5**]. Energies in kcal mol^{-1} (0 K + ZPE) at the G3X-K level of theory. Low-energy decomposition channels also indicated (a complete set of bond dissociation energies is provided as Supporting Information).

We have identified three separate pathways for the isomerization of hydroxyacetone and 2-hydroxypropanal. Firstly, these compounds are connected by the *E* isomer of their shared enediol form [**4**], through **TS4** and **TS5**. These reactions involve conventional keto-enol tautomerizations, with transition state barriers of around 70 kcal mol^{-1} relative to the carbonyl forms. A similar process also connects hydroxyacetone with its second enol structure [**2**], through **TS1**. Secondly, the *Z* enediol isomer can be accessed via **TS2** and **TS3**, with marginally lower barriers than in the prior mechanism. In this case reaction transpires via the simultaneous movement of two H atoms, mediated by the hydroxyl group. Thirdly, hydroxyacetone and 2-hydroxypropanal are found to be directly connected by **TS6**. This reaction again proceeds via the concerted transfer of two H atoms, and requires a barrier of only 43 kcal mol^{-1} relative to hydroxyacetone (39 kcal mol^{-1} relative to the higher-energy isomer 2-hydroxypropanal). This reaction provides the lowest energy mechanism by far for the interconversion of hydroxyacetone and 2-hydroxypropanal. The optimized structure for this key transition state is shown in Figure 2. Moreover, an intrinsic reaction coordinate scan was performed and the results are included as Figure 3. The process is seen to be highly concerted, with a 1,2 H-shift taking place as a 1,4 H-shift occurs between the O atoms.

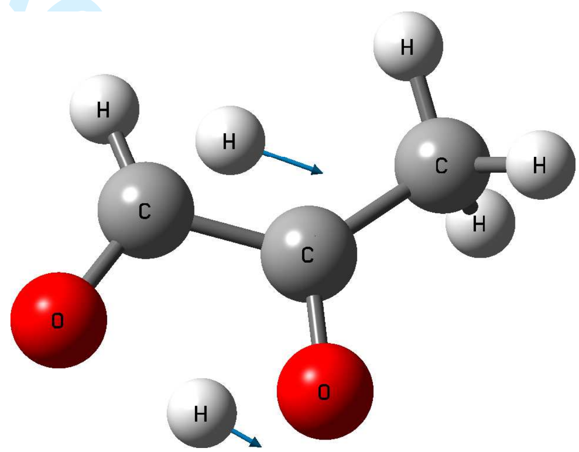

Figure 2. Optimized transition state structure for direct isomerization of hydroxyacetone and 2-hydroxypropanal (**TS6** in Figure 1), calculated at the M06-2X/6-31G(2df,p) level of theory. Displacement vectors included for the imaginary frequency.

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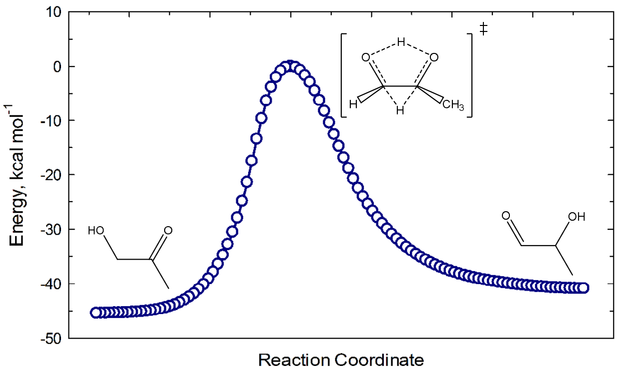

Figure 3. Intrinsic reaction coordinate scan for **TS6**, which directly connects hydroxyacetone (left) and 2-hydroxypropanal (right). Calculated at the M06-2X/6-31G(2df,p) level of theory.

The α-hydroxy carbonyl unit is endemic to open-chain monosaccharides, and the reaction described above therefore provides a new mechanism to explain aldose-ketone isomerizations. To this end we have examined the simplest such case: isomerization of the aldose glyceral with the ketose dihydroxyacetone. In this instance the additional OH group appears to stabilize the transition state, with an isomerization barrier of only 30.9 kcal mol^{-1} (36.6 kcal mol^{-1} in the dihydroxyacetone → glyceral direction). This adds to a large body of research on aldose-ketone isomerizations,[14,16-20] and in the gas-phase in the absence of catalysts this represents the most favorable mechanism. This mechanism should also be considered in future endavours evaluating catalytic aldose-ketose isomerization mechanisms.

Next, we have applied our mechanism to the isomerization of hydroxyl carbonyls with β-, γ-, and δ-OH groups, with the results shown in Figure 4. This effectively extends the mechanism up to tetrose, pentose, and hexose model compounds, thus incorporating the bulk of the open-chain monosaccharides. Figure 4 reveals that direct isomerization of the β-hydroxy carbonyls 3-hydroxy-1-butanal and 4-hydroxy-2-butanone still proceeds, albeit with a barrier of over 55 kcal mol^{-1}. The increase in barrier height relative to the β-OH analogues is attributed to ring strain in the transition state structure, induced by a 1,3 H-shift along the carbon backbone. When the hydrocarbon chain is further elongated, however, this ring strain is relieved considerably. For the isomerization of 4-hydroxy-1-propanal with 5-hydroxy-2-propanone (examples of γ-hydroxy carbonyls) the isomerization barrier drops to below 40 kcal mol^{-1}, whereas for the isomerization of 5-hydroxy-1-heptanal with 6-hydroxy-2-heptanone (δ-hydroxy carbonyls) the barrier is less than 30 kcal mol^{-1}.

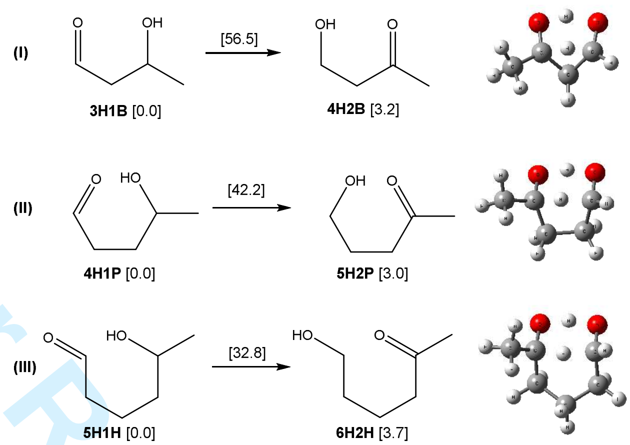

Figure 4. Isomerization mechanisms for the hydroxy-carbonyl compounds (I) 3-hydroxy-1-butanal (**3H1B**) and 4-hydroxy-2-butanone (**4H2B**), (II) 4-hydroxy-1-pentanal (**4H1P**) and 5-hydroxy-2-pentanone (**5H2P**), and (III) 5-hydroxy-1-heptanal (**5H1H**) and 6-hydroxy-2-heptanone (**6H2H**). Energies in kcal mol^{-1} (0 K) at the G3X-K level of theory. Transition state structures at the M06-2X/6-31G(2df,p) level of theory are shown at right.

The results presented above demonstrate that direct isomerization via a double hydride shift is a general mechanism for hydroxycarbonyls, and that these reactions will proceed with barriers that are readily surmountable in thermal systems. We now turn our attention to the kinetics of 2-hydroxypropanal / hydroxyacetone isomerization. So as to incorporate this reaction into kinetic models, we have calculated

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thermochemical properties and rate coefficients; thermochemical properties are listed in Table S1 of the Supporting Information, whereas rate coefficients and equilibrium constants are plotted in Figure S4. Inverse log plots of *k vs. T* are curved at low temperatures, due to tunnelling, but show good linearity above 500 K. Arrhenius fits between 500 K and 2000 K provide a pre-exponential factor of 6.19×10^{11} s^{-1} and activation energy of 37.2 kcal mol^{-1} for the isomerization of 2-hydroxpropanal to hydroxyacetone, with values of 2.27×10^{11} s^{-1} and 41.1 kcal mol^{-1} for the reverse process.

Finally, we consider the potential photoisomerization of 2-hydroxpropanal and hydroxyacetone. Hydroxycarbonyls are similar to the unsubstituted aldehydes and ketones in that they absorb solar radiation from around 320 to 220 nm.[21,22] Following solar excitation, if some fraction of the population undergoes internal conversion to the ground state then it will possess 90 kcal mol^{-1} (~ 30 000 cm^{-1}) or more of additional vibrational energy which can go into molecular fragmentation and isomerization processes. This energy is more than sufficient to surmount the isomerization barrier between hydroxyacetone and 2-hydroxypropanal. This process would open up new dissociation channels following isomerization and may permit collisional deactivation as the isomeric form, as has been found for acetaldehyde, which tautomerizes to the enol form (where the barrier is ~ 70 kcal mol^{-1}),[23,24] in addition to processes mediated by the excited state and triplet maifolds. To gain insight into the potential phtoisomerization process, RRKM theory has been used to calculate $k(E)$ values for interconversion between hydroxyactone and 2-hydroxypropanal, and they are plotted in Figure S5. At the energies we are concerned with $k(E) > 10^8$ s^{-1}, which is commensurate with the timescale for collisional deactivation under tropospheric conditions (see, for example, ref. [25]). Accordingly, these species should equilibrate prior to collisional deactivation, and their photoisomerization (as well as that of other hydroxycarbonyls) may be a significant atmospheric process.

Methods

Electronic structure theory calculations were carried out using the Gaussian 09 code.[26] Geometry optimization and vibrational frequency calculations were performed at the M06-2X/6-31G(2df,p) density functional level of theory. These structures were used in subsequent single-point wavefunction theory energy calculations in order to obtain the composite G3X-K energy.[27] The G3X-K method is designed specifically for thermochemical kinetics, and provides barrier heights to an accuracy of around 0.6 kcal mol^{-1}, on average. Reported energies are at 0 K and include the zero point vibrational energy, unless otherwise stated. Thermochemical properties, canonical rate coefficients $k(T)$, and microscopic rate coefficients $k(E)$, were calculated from statistical mechanical principles, canonical transition state theory, and RRKM theory, using the MultiWell program suite.[28,29] Quantum mechanical tunnelling corrections are included in rate constant calculations, and the low-energy C–C(O) internal rotational mode is treated as a free rotor.

Acknowledgments

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Keywords: Computational chemistry; gas-phase reactions; pyrolysis; reaction mechanisms

((Additional Supporting Information may be found in the online version of this article.))

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GRAPHICAL ABSTRACT

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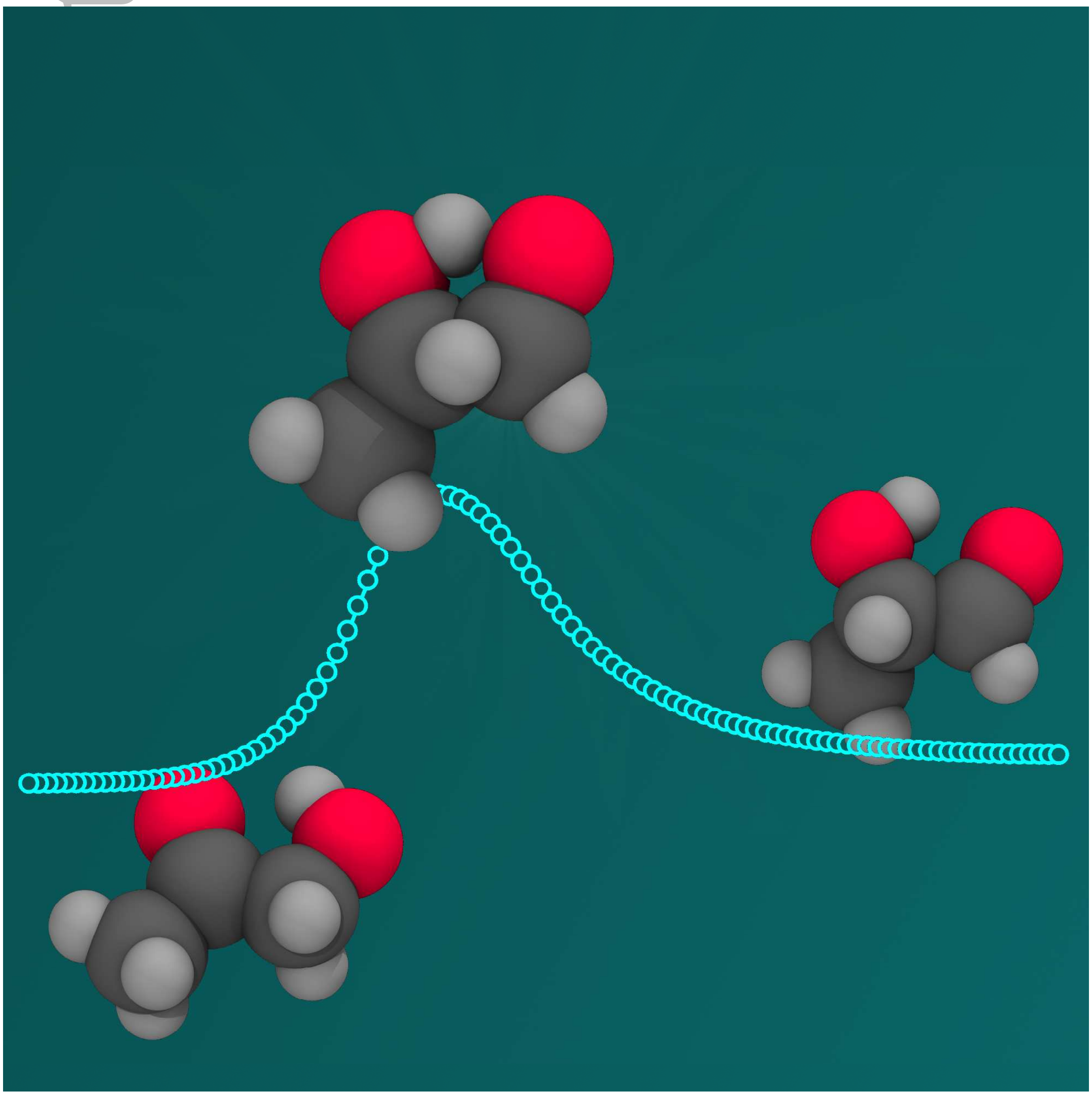
The Gas Phase Aldose-Ketose Isomerization Mechanism: Direct Interconversion of the Model Hydroxycarbonyls 2-Hydroxpropanal and Hydroxyacetone

Hydroxycarbonyl compounds can be directly interconverted with a low barrier via a double hydride transfer mechanism. This process explains gas-phase aldose-ketose isomerization in simple sugars and provides new insights intp hydroxycarbonyl chemistry in the atmosphere and in the thermochemical processing of carbohydrates



SUPPORTING INFORMATION

The Gas-Phase Aldose-Ketose Isomerization Mechanism: Direct Interconversion of the Model Hydroxy-Carbonyls 2-Hydroxpropanal and Hydroxacetone

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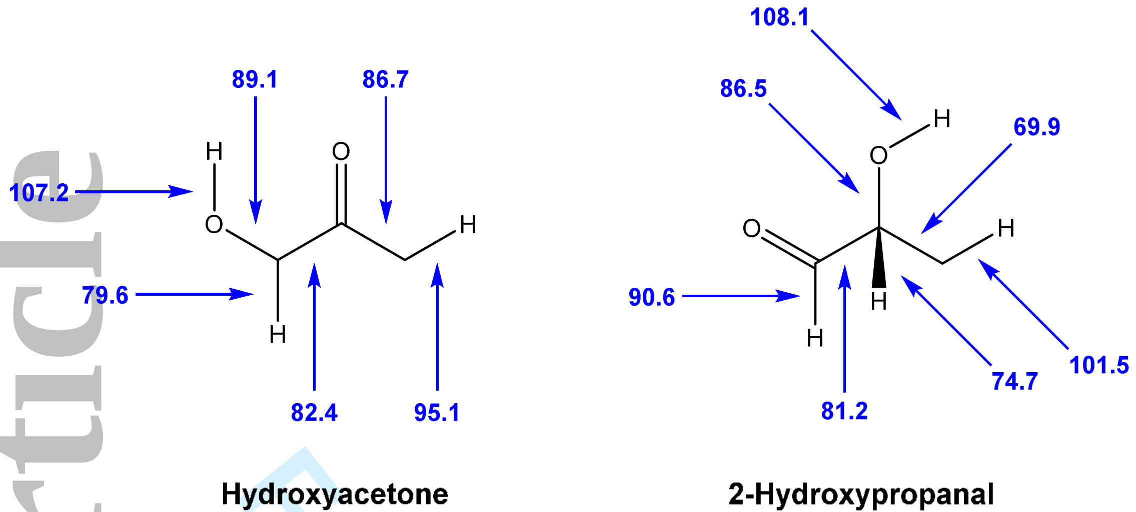


Figure S1. Bond dissociation energies in hydroxyacetone and 2-hydroxypropanal. Energies in kcal mol^{-1} (0 K) at the G3X-K level of theory.

1 **2** **3** **4** **5**

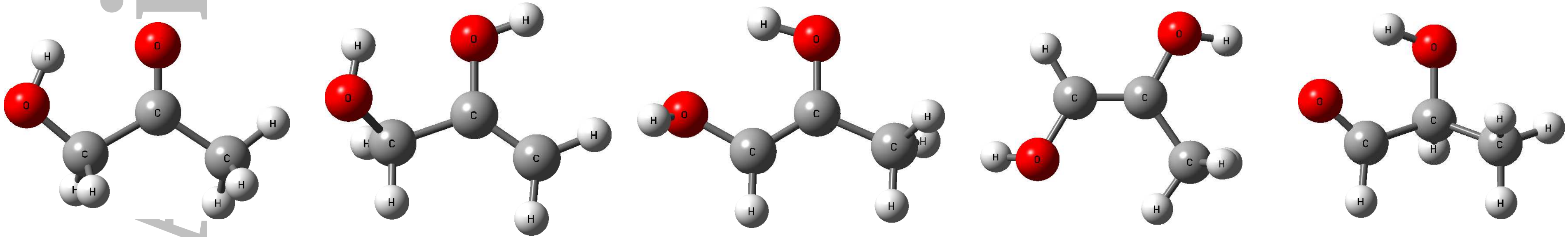


Figure S2. Optimized structures for $C_3O_2H_6$ minima in the reaction mechanism shown in Figure 1, calculated at the M06-2X/6-31G(2df,p) level of theory.

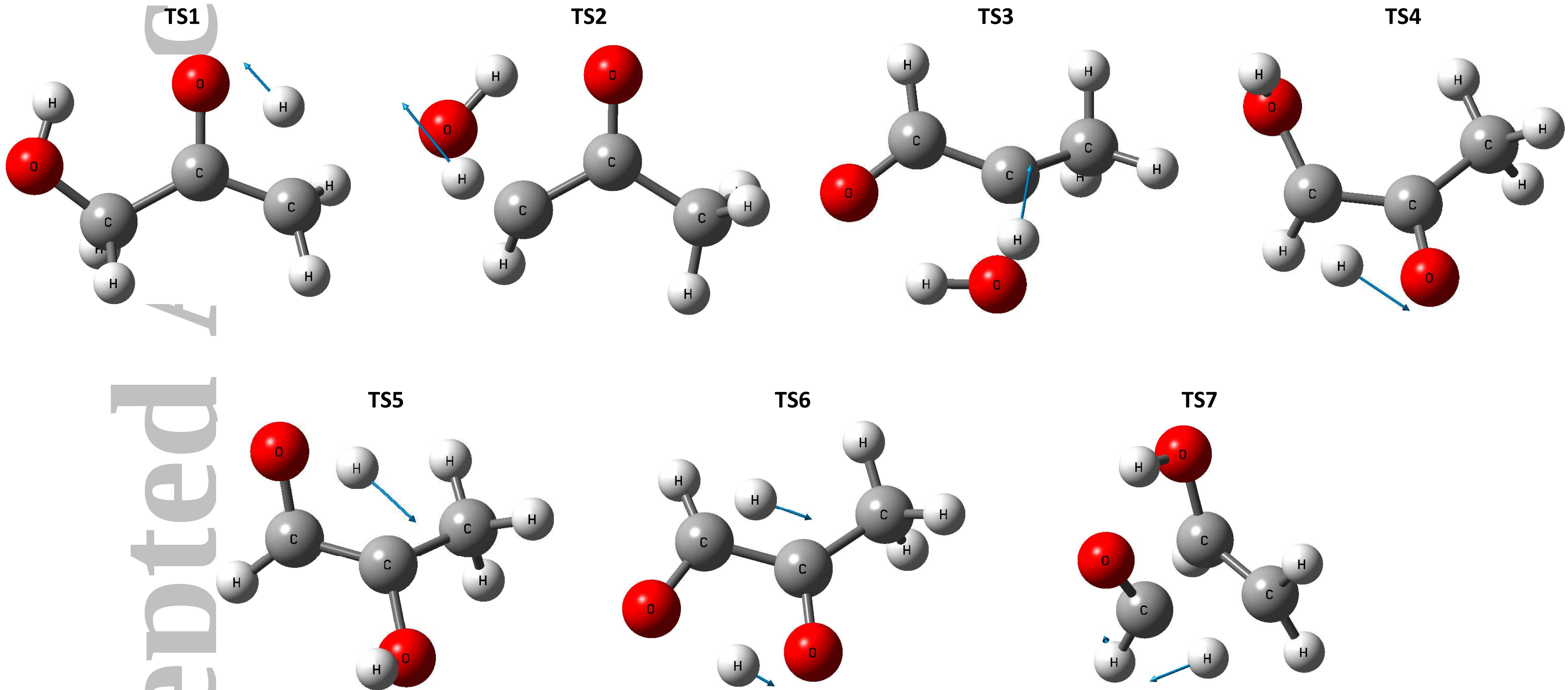
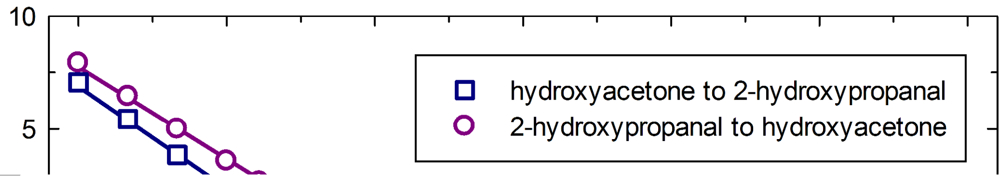


Figure S3. Optimized structures for transition states in the reaction mechanism shown in Figure 1, calculated at the M06-2X/6-31G(2df,p) level of theory. Displacement vectors included for imaginary frequencies.


10
5
hydroxyacetone to 2-hydroxypropanal
2-hydroxypropanal to hydroxyacetone

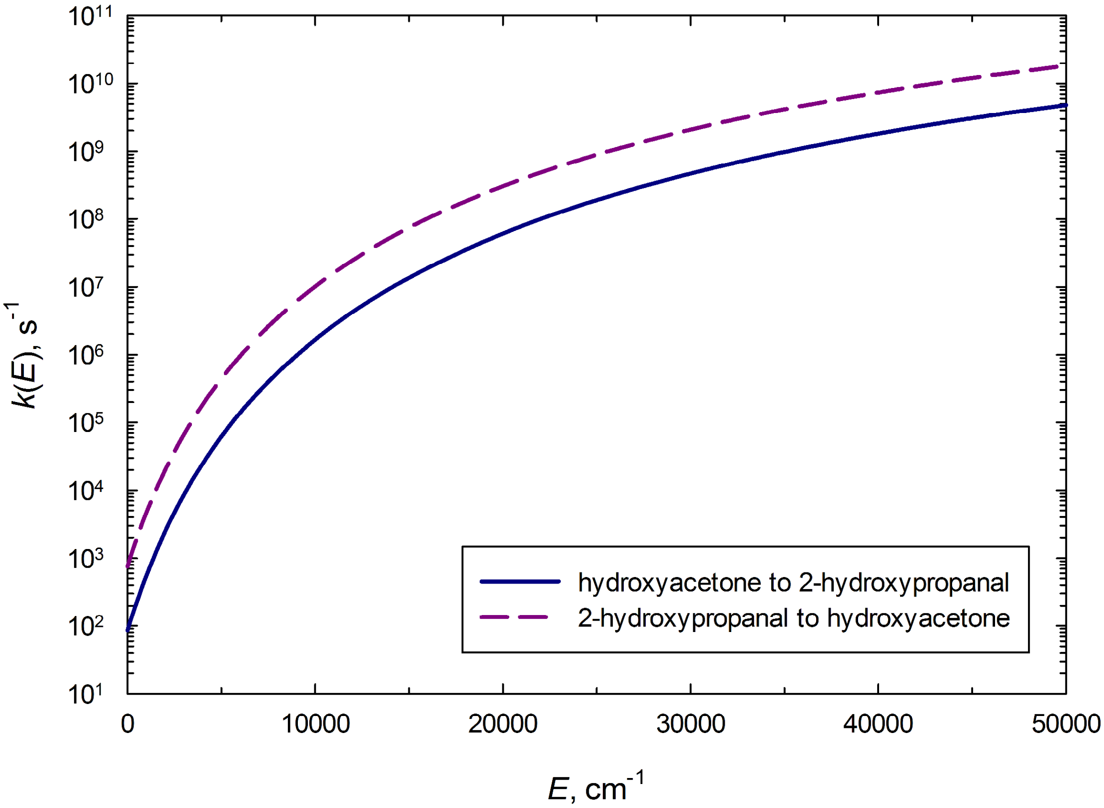


Figure S5. RRKM theory rate coefficients, $k(E)$ [s^{-1}], for isomerization of hydroxyacetone with 2-hydroxypropanal via **TS6**, as a function of active internal energy, E.

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Table S1. Standard enthalpies of formation ($\Delta_f H°_0$ and $\Delta_f H°_{298}$, kcal mol^{-1}), entropies ($S°_{298}$, cal mol^{-1} K^{-1}), and heat capacities ($C_p(T)$, cal mol^{-1} K^{-1}), for hydroxyacetone and 2-hydroxpropanal.

	$\Delta_f H°_0$	$\Delta_f H°_{298}$	$S°_{298}$	$C_p(300)$	$C_p(400)$	$C_p(500)$	$C_p(600)$	$C_p(800)$	$C_p(1000)$	$C_p(1500)$	$C_p(2000)$
Hydroxyacetone [**1**]	-84.5	-89.2	80.46	20.94	25.76	30.16	33.93	39.84	44.18	50.93	54.44
2-Hydroxypropanal [**5**]	-80.3	-83.9	78.60	20.64	25.56	30.03	33.85	39.82	44.19	50.96	54.46

Cartesian Coordinates (Å)

1			
C	0.46996	0.16511	-0.00937
C	-0.72343	-0.77563	-0.02116
H	-0.64918	-1.39523	-0.92898
H	-0.62659	-1.46311	0.83290
O	-1.92227	-0.07642	0.02402
O	0.28226	1.35639	-0.00895
H	-1.67433	0.85872	0.01054
C	1.84301	-0.45439	0.01093
H	2.00942	-0.92819	0.98304
H	1.92513	-1.23530	-0.74929
H	2.59834	0.31286	-0.15126

2			
C	0.79902	-0.61592	0.39474
C	-0.55533	-0.04873	0.07553
O	1.80555	-0.03714	-0.39936
H	0.80183	-1.69076	0.20626
O	-0.49873	1.31131	0.13454
C	-1.64164	-0.75540	-0.20658
H	-1.59093	-1.83363	-0.25323
H	-2.60103	-0.28616	-0.39402
H	1.67183	0.91453	-0.35933
H	0.99835	-0.45594	1.46591
H	-1.34691	1.67888	-0.12916

3			
C	0.42822	0.00582	0.00861
C	-0.68012	-0.73004	-0.00558
O	-1.90329	-0.08693	-0.09115
O	0.37917	1.36226	0.01201
H	-2.46391	-0.38537	0.62930
H	-0.66811	-1.81277	-0.03111
H	-0.55696	1.59880	-0.01067
C	1.81315	-0.54081	0.00345
H	2.34976	-0.20669	-0.88887
H	2.36451	-0.17539	0.87415
H	1.80019	-1.63105	0.02150

4

C	0.78283	-0.64552	-0.01984
C	-0.42966	-0.10458	-0.01451
O	-1.51575	-0.93998	0.04758
O	1.91209	0.13023	0.08161
H	-2.28446	-0.45957	-0.26716
H	0.90610	-1.72463	-0.02152
H	2.59126	-0.24687	-0.48107
C	-0.69792	1.36448	-0.00647
H	-1.21149	1.66037	0.91398
H	0.23695	1.91793	-0.08258
H	-1.34058	1.64444	-0.85022

5

C	0.84676	-0.67415	0.20609
C	-0.44379	0.08260	0.42399
O	1.81582	-0.15274	-0.27578
H	0.84863	-1.73988	0.50975
O	-0.31937	1.39590	-0.02529
H	0.59683	1.49502	-0.31783
C	-1.59336	-0.63414	-0.28317
H	-1.40741	-0.66638	-1.35921
H	-1.71497	-1.65402	0.09150
H	-2.51963	-0.08542	-0.10859
H	-0.63269	0.05953	1.51147

TS1

C	0.83168	-0.74433	0.12523
C	-0.48209	-0.04106	0.02886
O	1.92409	0.08336	-0.12893
H	0.87072	-1.18691	1.13460
C	-1.79524	-0.53667	-0.11027
H	-2.42118	-0.28369	0.74496
H	-1.99899	-1.50828	-0.54475
H	-1.65899	0.91903	-0.33346
O	-0.49614	1.24016	0.03877
H	0.82379	-1.58366	-0.58018
H	1.63498	0.98766	0.03714

TS2

C	-0.57328	-0.88610	0.07891
C	0.46310	0.09045	0.00825
H	-1.56891	-0.55493	0.88199
C	1.89862	-0.35446	-0.00675
H	1.98857	-1.44020	0.04816
H	2.42405	0.09752	0.83685
H	2.37076	0.00645	-0.92330
O	0.14940	1.28837	-0.00034
O	-1.88964	-0.07051	-0.08628
H	-1.42700	0.83338	-0.11130
H	-0.59611	-1.78453	-0.52194

TS3

C	0.44594	-0.07020	-0.32262
C	-0.74348	-0.81124	-0.10652
H	0.17167	1.04568	-1.00135
O	-1.80890	-0.24897	0.16386
O	0.04405	1.40291	0.05830
H	-0.91588	1.19843	0.28243
C	1.80897	-0.43670	0.15487
H	1.97035	-1.49524	-0.07024
H	2.59419	0.13063	-0.34772
H	1.91648	-0.29780	1.23658
H	-0.68663	-1.90442	-0.23140

TS4

C	0.82953	-0.53065	0.17852
C	-0.52154	-0.09470	0.03237
H	-0.07763	-1.61352	-0.26127
C	-1.07117	1.28388	0.03301
H	-0.25230	2.00332	0.01298
H	-1.64337	1.41748	0.95666
H	-1.74971	1.44373	-0.80619
O	-1.24541	-1.13011	-0.13936
O	1.89642	0.33319	-0.05162
H	2.16029	0.23599	-0.96794
H	0.93366	-1.06281	1.13015

TS5

C	0.90490	-0.47053	0.41356
C	-0.34185	-0.09219	-0.15818
H	0.86288	0.29240	-0.98183
O	1.86229	0.05940	-0.23978
H	1.11955	-1.15911	1.23567
O	-1.43137	-0.95565	-0.04981
H	-1.27711	-1.70886	-0.62228
C	-0.79467	1.34025	0.10536
H	-1.39836	1.36951	1.02002
H	0.05358	2.01714	0.21870
H	-1.41817	1.69380	-0.71797

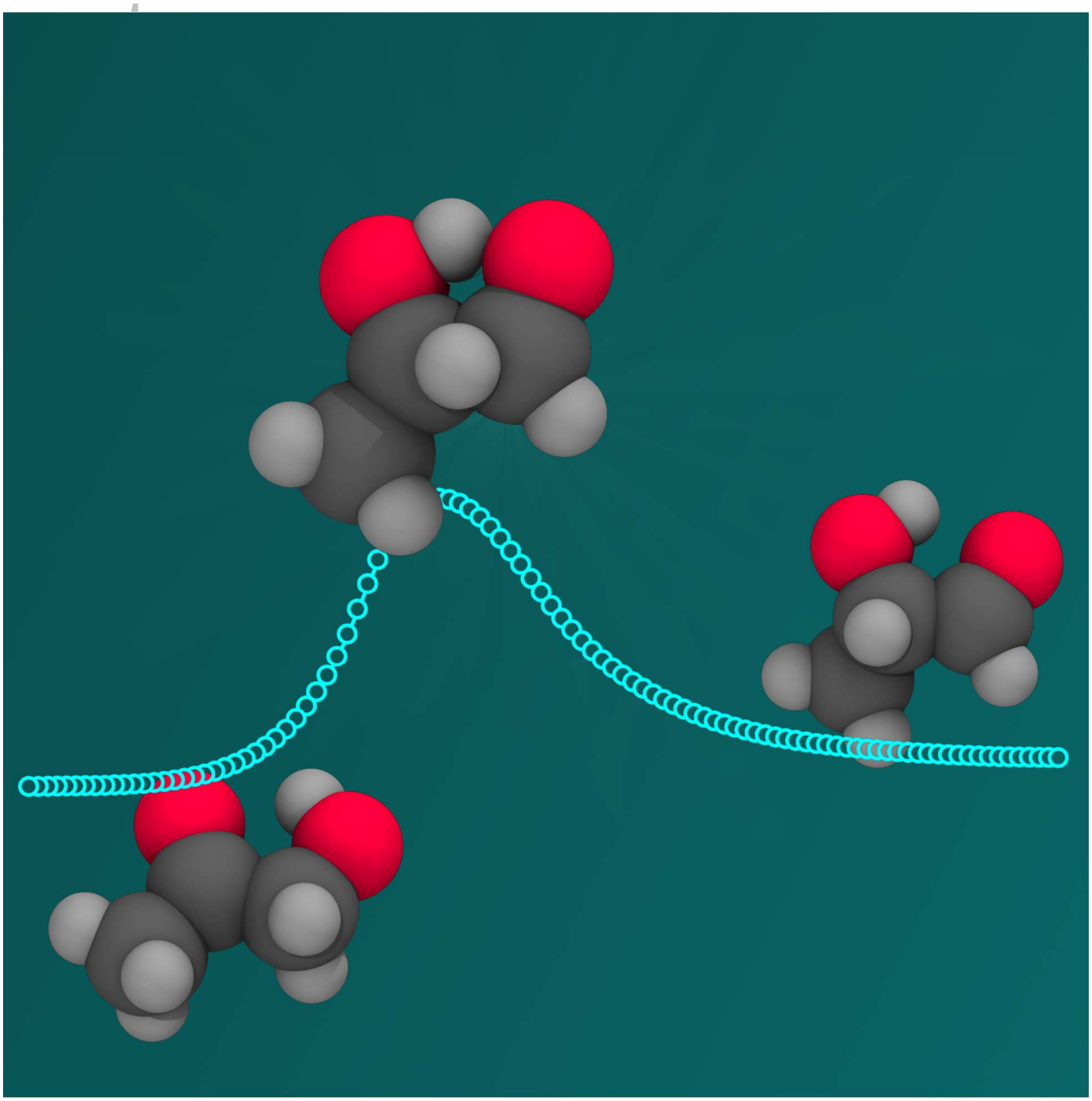
TS6

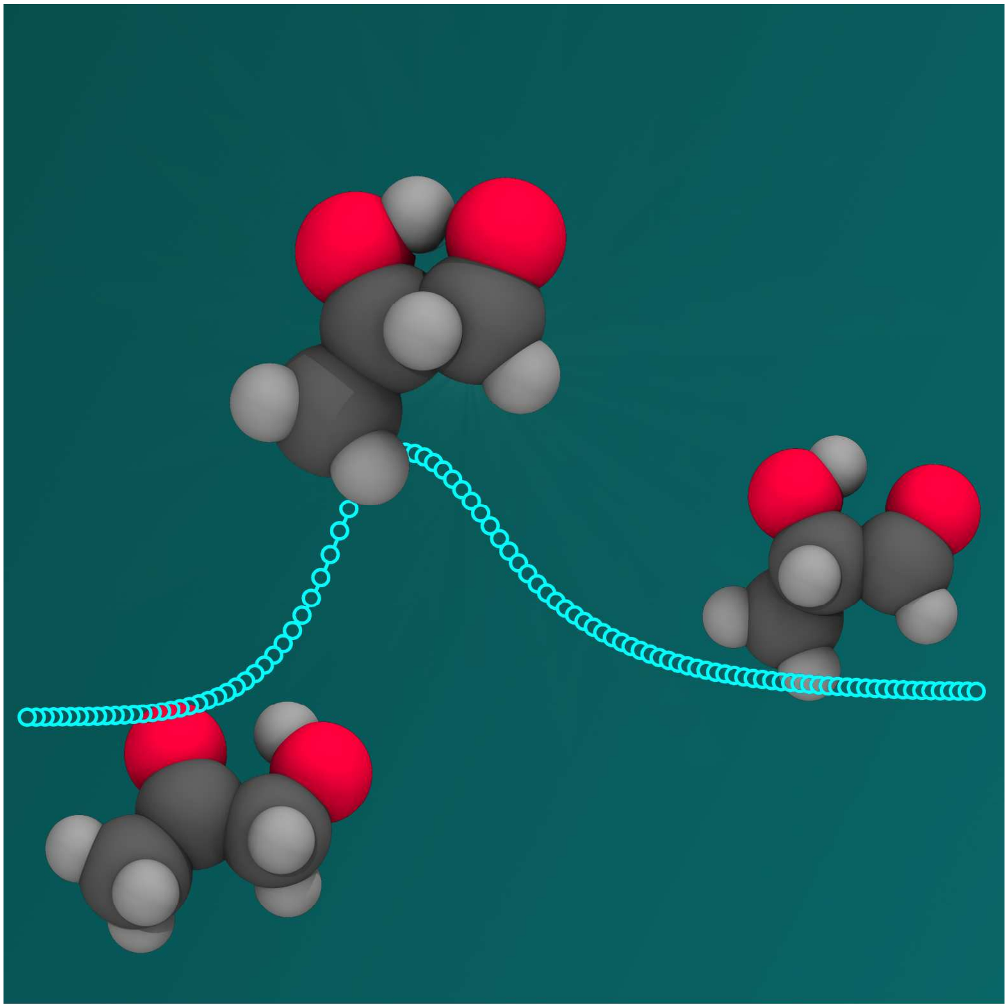
C	-1.85782	-0.34732	-0.05571
C	-0.42948	0.05349	0.00817
H	0.13822	-0.76098	1.16223
C	0.74732	-0.79011	0.00317
H	0.66085	-1.85743	-0.22143
O	1.83045	-0.12013	-0.07054
H	0.99311	1.09227	-0.05973
O	-0.06813	1.28870	0.02704
H	-2.24236	-0.07468	-1.04215
H	-1.96073	-1.42506	0.08094
H	-2.44783	0.18103	0.69438

TS7

C	0.77492	-0.54867	0.36412
C	-0.81867	0.12340	0.41431
O	1.53273	0.25444	-0.23089
H	0.88418	-1.00272	1.35337
H	-1.26832	0.07012	1.40092
C	-0.85513	-1.04096	-0.41364
H	-0.76911	-0.91145	-1.48796
H	-1.29363	-1.96247	-0.04233
H	0.54591	-1.59598	-0.24338
O	-0.66214	1.34938	-0.12612
H	0.32955	1.36929	-0.31331

Hydroxycarbonyl compounds can be directly interconverted with a low barrier via a double hydride transfer mechanism. This process explains gas-phase aldose-ketose isomerization in simple sugars and provides new insights into hydroxycarbonyl chemistry in the atmosphere and in the thermochemical processing of carbohydrates





Suggested cover art

251x251mm (300 x 300 DPI)