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Thermochemistry of Simple Enols and Enol Cation Radicals Revisited. A G2(MP2) ab Initio Study

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Abstract: Simple enols, vinyl alcohol (**1**), propen-2-ol (**2**), (*E*)-propen-1-ol (**3**), (*Z*)-propen-1-ol (**4**), (*E*)-2-buten-2-ol (**5**), and (*Z*)-2-buten-2-ol (**6**), and their cation radicals are investigated by ab initio calculations at the Gaussian 2 (MP2) level of theory. Syn-planar conformations are found to be thermodynamically more stable for gaseous **1**, **2**, **3**, **5**, and **6**, which give ΔG°_{298}(anti−syn) = 2.5, 4.0, 1.4, 5.6, and 3.3 kJ mol^{-1}, respectively. The syn form of **4** is thermochemically favored by ΔH°_{298}(anti−syn) = 1.2 kJ mol^{-1}, but disfavored by entropy, which leads to ΔG°_{298}(anti−syn) = −0.5 kJ mol^{-1}. The enols are predicted to exist as mixtures of rotamers in the gas phase. Standard enthalpies of formation for **1**, **2**, **3**, **4**, **5**, and **6** are calculated from isodesmic reactions as −123, −167, −147, −148, −190, and −195 kJ mol^{-1}, respectively. Enol cation radicals uniformly prefer anti conformations with ΔG°_{298}(syn−anti) = 3.5−8.1 kJ mol^{-1}. Standard enthalpies of formation from isodesmic and isogyric reactions were calculated as 765, 677, 682, 682, 603, and 601 kJ mol^{-1} for $\mathbf{1}^{\bullet+}$, $\mathbf{2}^{\bullet+}$, $\mathbf{3}^{\bullet+}$, $\mathbf{4}^{\bullet+}$, $\mathbf{5}^{\bullet+}$, and $\mathbf{6}^{\bullet+}$, respectively. The calculated $\Delta H^\circ_{f,298}$ show good agreement with experimental estimates for **1** and $\mathbf{1}^{\bullet+}$, but diverge for the higher enols. The divergence is significantly diminished when 298 K enthalpy corrections are included in the experimental threshold energies. The calculated adiabatic ionization energies are in excellent to fair agreement with experimental data for **1**, **2**, **3**, and **4**, but show 0.2−0.3 eV deviations for **5** and **6**.

Simple enols, $R_1R_2C{=}C(R_3){-}OH$, represent important intermediates in a variety of organic reactions as summarized recently.[3] First proposed in 1881 by Erlenmeyer,[4] enols have been the subject of numerous experimental and theoretical studies.[5] Solution enol−oxo equilibrium measurements[5] and the kinetic studies of Kresge, Keeffe, and co-workers[6] yielded relative free energies for the solvated enol−oxo systems in which enols were as a rule the less stable isomers.[7] By contrast, gas-phase thermochemistry of enols has relied mostly on thermochemical cycles combining the enthalpies of formation (ΔH_f) of enol cation radicals[8] with the threshold ionization energies of neutral enols generated transiently in the rarefied gas phase.[9,10] Thermochemistry of enol cation radicals represents an essential part of gas-phase ion chemistry.[8,11] Cation radicals derived from simple enols are as a rule more stable than their aldehyde, ketone, or other valence-bond isomers.[8,11]

The stabilities of enol molecules[12] and cation radicals[13] relative to their aldehyde or ketone counterparts have been investigated by semiempirical and ab initio calculations, which pointed out some fundamental properties of these species, as summarized by Apeloig.[14] It is known from experiment[15] and confirmed by theory[14] that simple enols prefer planar syn conformations in the gas phase, whereas enol cation radicals are predicted to be more stable as anti rotamers.[13a,b] Simple enols have been calculated by semiempirical and ab initio methods to be less stable than their oxo counterparts, although the enthalpy differences depended on the method used and often differed from the experimental estimates.[14] The most extensive calculations carried out so far by Radom and co-workers predicted vinyl alcohol to be destabilized against acetaldehyde by 47 kJ mol^{-1}.[16] Substituent effects on the enol stability and

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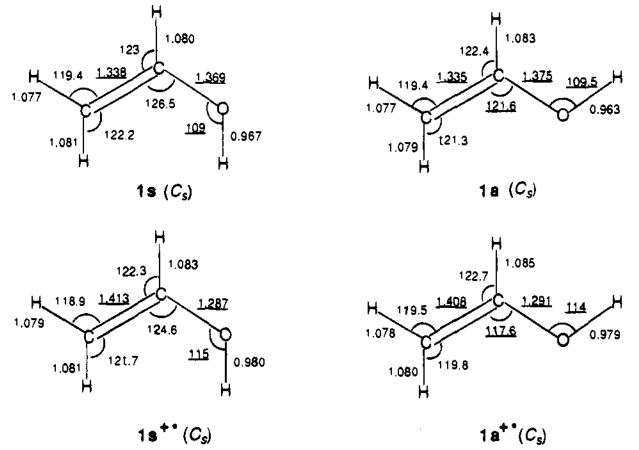

Figure 1. MP2(FULL)/6-31+G(d,p) optimized geometries of **1s**, **1s**$^{\bullet+}$, **1a**, and **1a**$^{\bullet+}$. Bond lengths in angstroms, bond angles in degrees.

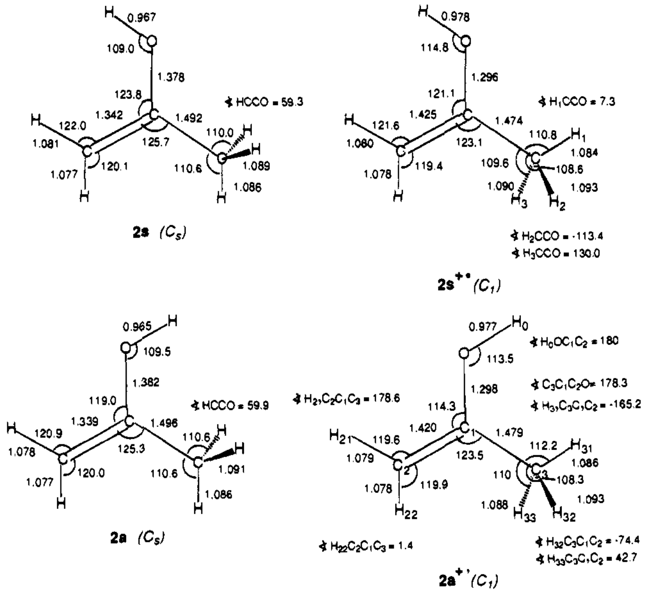

Figure 2. MP2(FULL)/6-31+G(d,p) optimized geometries of **2s**, **2s**$^{\bullet+}$, **2a**, and **2a**$^{\bullet+}$.

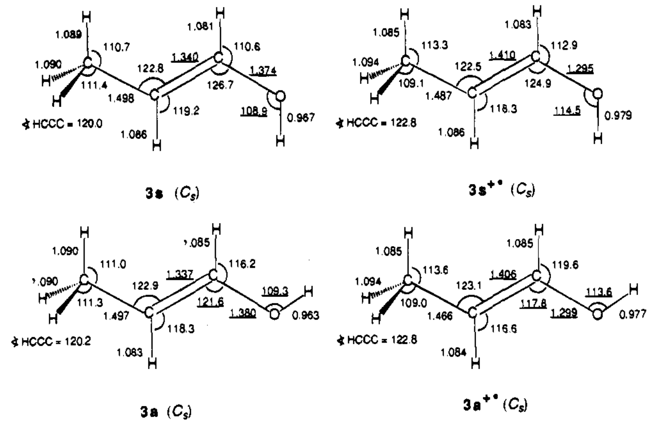

Figure 3. MP2(FULL)/6-31+G(d,p) optimized geometries of **3s**, **3s**$^{\bullet+}$, **3a**, and **3a**$^{\bullet+}$.

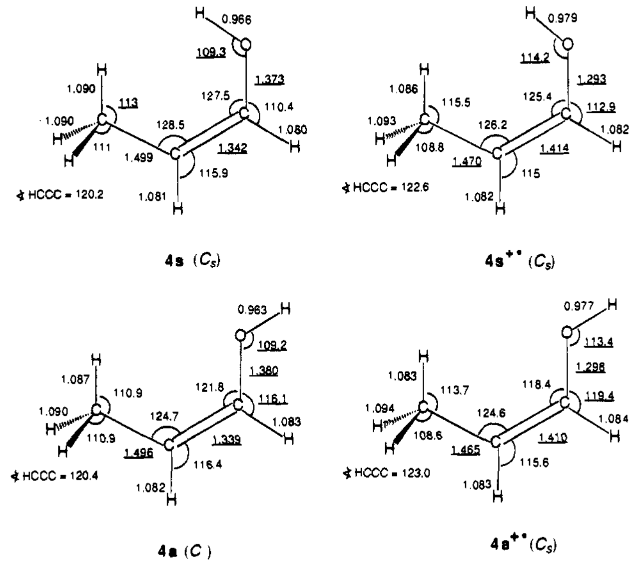

Figure 4. MP2(FULL)/6-31+G(d,p) optimized geometries of **4s**, **4s**$^{\bullet+}$, **4a**, and **4a**$^{\bullet+}$.

electron distribution have been investigated by Apeloig,[12e] Schwarz,[12g] and their co-workers at medium levels of ab initio theory.

In spite of a wealth of data on enol structures and thermochemistry, there remain several unresolved problems of a fundamental nature. First, the populations of enol rotamers have not been studied experimentally nor determined computationally to aid interpretation of ionization energies from threshold measurements[9,10] and photoelectron spectra.[17] In particular, distinction of adiabatic and vertical ionization energies in rotamer mixtures is difficult if not impossible at present.[17] Second, inconsistencies appear to exist in the enthalpies of formation of enol cation radicals, which provide reference data for the thermochemistry of neutral enols[8-10] and other gas-phase cations as well.[11,13,14] The ΔH_f values for enol cation–radicals have been obtained from threshold appearance energy measurements utilizing unimolecular ion dissociations, in which temperature is poorly defined, and conversion to the standard state is thus difficult.[18] Third, most of the enol ionization energies have been obtained by threshold electron impact measurements, which have not been verified by more accurate spectroscopic methods, such as photoelectron,[17] photoionization,[18] or zero electron kinetic energy spectroscopy.[19] Last but not least, the previous ab initio calculations, mostly carried out with basis sets of a split-valence double-ζ quality,[14] did not bring accurate ionization energies to interconnect the neutral and cation-radical energies, which existed as separate sets of data,

The objective of this work is to provide a comprehensive treatment of simple neutral enols and their cation radicals at a uniformly high level of ab initio theory, following the recent work by Radom and co-workers.[16] The Gaussian 2 (G2) scheme of Pople and co-workers[20a] and its modified versions[20b,c] have been shown to provide accurate relative enthalpies and ionization energies for a variety of molecules, and have been instrumental in pointing out inconsistencies in experimental data, such as the structure of gaseous vinyl alcohol,[21] and the proton affinity scale.[22] Here we apply the G2(MP2) scheme, which is augmented in the geometry optimization procedure, to obtain

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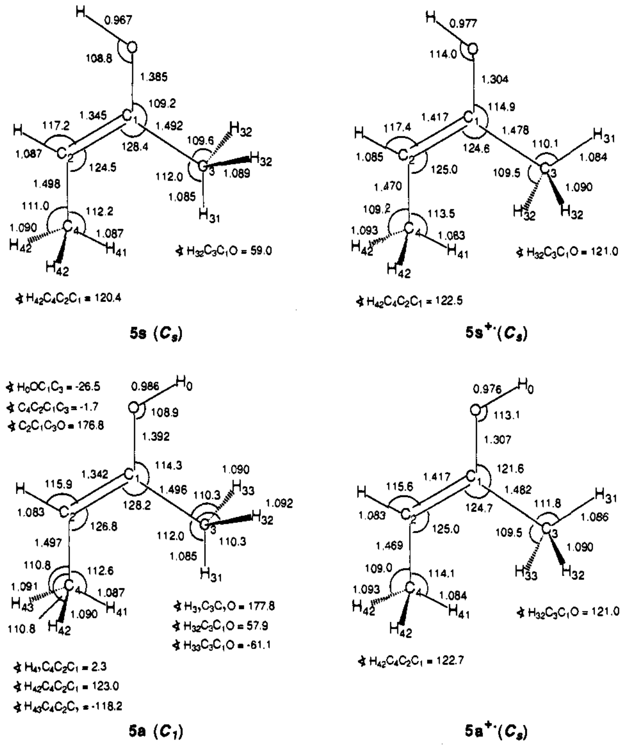
5s (C_s) **5s**$^{•+}$(C_s) **5a** (C_1) **5a**$^{•+}$(C_s)

Figure 5. MP2(FULL)/6-31+G(d,p) optimized geometries of **5s**, **5s**$^{•+}$, **5a**, and **5a**$^{•+}$.

equilibrium structures for syn and anti rotamers of vinyl alcohol (**1s** and **1a**, respectively), *syn-* and *anti*-propen-2-ols, **2s** and **2a**, *syn-* and *anti-*(*E*)-prop-1-en-1-ols, **3s** and **3a**, *syn-* and *anti-*(*Z*)-prop-1-en-1-ols, **4s** and **4a**, *syn-* and *anti-*(*E*)-but-2-en-2-ols, **5s** and **5a**, and *syn-* and *anti-*(*Z*)-but-2-en-2-ols, **6s** and **6a**, as well as their corresponding cation radicals **1s**$^{•+}$ and **1a**$^{•+}$ through **6s**$^{•+}$ and **6a**$^{•+}$. We evaluate the enthalpies of isodesmic and isogyric reactions involving the enols to obtain relative enthalpies that are anchored to standard thermochemical data to provide $\Delta H°_{f,298}$ values for neutral enols and their cation radicals. We also calculate adiabatic and vertical ionization energies that are compared with the experimental data and used to interpret the results of previous ionization energy measurements.[10,17]

Calculations

Standard ab initio calculations were carried out using the Gaussian 92[23] and Gaussian 94[24] suites of programs. Geometries were optimized using the 6-31+G(d,p) basis set at two levels, Hartree–Fock (HF), and employing all-electron Møller–Plesset perturbation theory[25] truncated at second order, MP2(FULL)/6-31+G(d,p), to estimate the correlation energy.[20] The use of diffuse atomic orbitals in the optimizations was motivated by the significant net negative charge on the oxygen and C_β carbon atoms in neutral enols.[8b,12c,g] Spin unrestricted (UHF) wave functions were used for the cation radicals. The unprojected $\langle S^2\rangle$ values were within 0.75–0.77 indicating negligible spin contamination. Spin annihilation methods[26] further reduce the $\langle S^2\rangle$ values; however, the corrections due to spin projection[26b] to the approximated QCISD(T)/6-311+G(3df,2p) energies were within 0.15 mhartrees for all cation radicals except $CH_3OH^{•+}$ (0.35 mhartree), which affected the calculated ionization energies and reaction enthalpies by 0.004 eV and 0.3 kJ mol^{-1}, respectively. Hence, unprojected total energies were employed throughout. Harmonic frequencies were calculated with HF/6-31+G(d,p) for all enols, and also with MP2-(FULL)/6-31+G(d,p) for **1s**, acetaldehyde, **1a**$^{•+}$, acetaldehyde$^{•+}$, **2s**, and acetone. The HF frequencies were corrected by 0.8923[27] and used to calculate zero-point vibrational energies. Enthalpies and entropies were calculated within the rigid-rotor harmonic oscillator (RRHO) model. Torsional modes were treated as low-frequency vibrations with a few exceptions of very low frequencies, which were considered as free internal rotations, as discussed later. Torsion about the C–O bond in vinyl alcohol was also treated as a two-maximum hindered rotation according to Pitzer,[28] which gave thermodynamic functions very similar to those from the RRHO treatment, as discussed below. Improved energies were obtained from single-point calculations at the MP2/6-311+G(3df,2p)[29] and QCISD(T)/6-311G(d,p)[30] levels of theory using the MP2(FULL)/6-31+G(d,p) geometries. The single-point energies were combined according to eq 1 to approximate QCISD(T)/6-311+G-(3df,2p) calculations similar to the G2(MP2) scheme.[20b] Empirical isogyric corrections inherent to the G2(MP2) scheme[20] cancel out in the isodesmic and isogyric reactions used to evaluate neutral and ion thermochemistry. The total energies obtained from eq 1 are summarized in Tables 1–4.

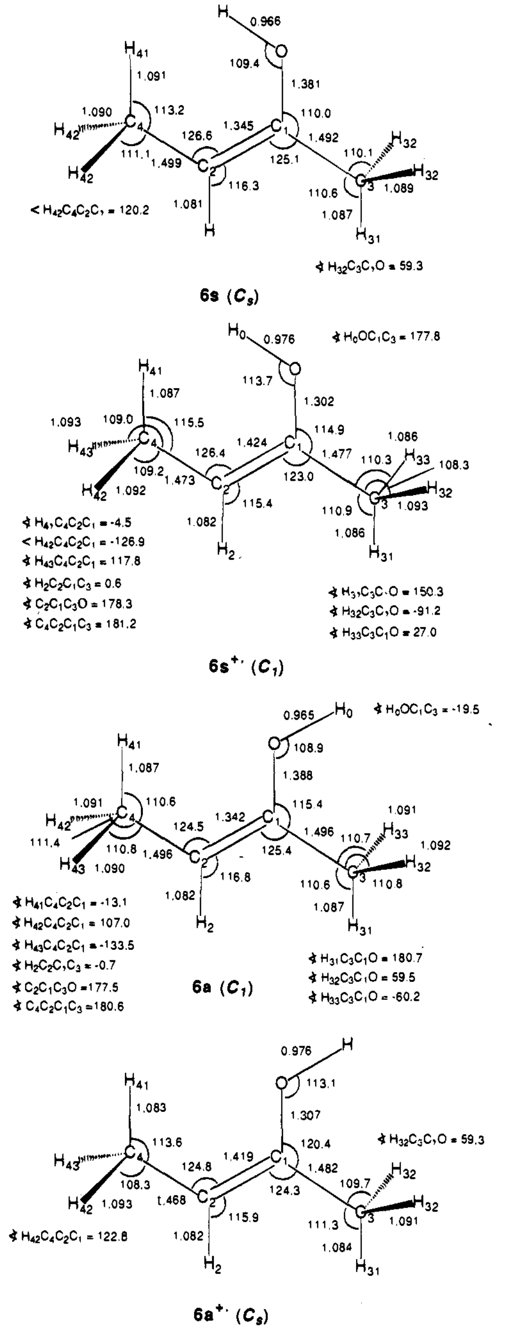
6s (C_s) **6s**$^{•+}$ (C_1) **6a** (C_1) **6a**$^{•+}$ (C_s)

Figure 6. MP2(FULL)/6-31+G(d,p) optimized geometries of **6s**, **6s**$^{•+}$, **6a**, and **6a**$^{•+}$.

$$E\{\text{QCISD(T)/6-311+G(3df,2p)}\} \approx E\{\text{QCISD(T)/6-311G(d,p)}\} + E\{\text{MP2/6-311+G(3df,2p)}\} - E\{\text{MP2/6-311G(d,p)}\} \quad (1)$$

To gauge the effects of aqueous solvation in certain instances,

Table 1. Ab Initio Total Energies for the Vinyl Alcohol Isomers and Auxiliary Molecules[a]

species	MP2(FULL)/ 6-31+G(d,p)	MP2/ 6-311G(d,p)	MP2/ 6-311+G(3df,2p)	QCISD(T)/ 6-311G(d,p)	QCISD(T)/ 6-311+G(3df,2p)[b]	ZPVE[c]	$H_{298} - H_0$[c]
syn-vinyl alcohol (**1s**)	−153.381 660	−153.422 349	−153.520 989	−153.466 177	−153.564 818	142.4	12.2
						142.1[d]	12.4[d]
anti-vinyl alcohol (**1a**)	−153.379 183	−153.419 036	−153.518 872	−153.463 191	−153.563 028	141.2	13.0
syn-vinyl alcohol$^{\bullet+}$ (**1s**$^{\bullet+}$)	−153.049 250	−153.091 694	−153.179 856	−153.138 001	−153.226 163	141.4	12.3
syn-vinyl alcohol$^{\bullet+}$(N)[e] (**1s**$^{\bullet+}$(N)[e])		−153.079 822	−153.168 408	−153.126 700	−153.215 286		
anti-vinyl alcohol$^{\bullet+}$ (**1a**$^{\bullet+}$)	−153.053171	−153.095 187	−153.183 117	−153.141 169	−153.229 099	141.7	12.2
						143.3[d]	12.2[d]
anti-vinyl alcohol$^{\bullet+}$(N)[e] (**1a**$^{\bullet+}$(N)[e])		−153.082 507	−153.170 903	−153.129 240	−153.217 636		
CH_3CHO	−153.402 250	−153.442 244	−153.538 00	−153.485 606	−153.581 362	139.2	12.9
						140.9[d]	12.9[d]
$CH_3CHO^{\bullet+}$	−153.017 811	−153.062 467	−153.147 078	−153.121 172	−153.205 783	135.5	13.2
						136.3[d]	13.3[d]
CH_4	−40.371 223	−40.379 166	−40.405 704	−40.405 732	−40.432 270	110.7	10.0
CH_3OH	−115.401 643	−115.436 068	−115.513 804	−115.468 560	−115.546 296	128.9	11.3
$CH_3OH^{\bullet+}$	−114.997 342	−115.037 924	−115.101 438	−115.081 372	−115.144 886	122.0	11.0
C_2H_4	−78.333 262	−78.344 231	−78.393 364	−78.384 047	−78.433 180	127.4	10.5
$C_2H_4^{\bullet+}$	−77.957 543	−77.965 931	−78.007 382	−78.006 395	−78.047 846	123.4	11.4
C_2H_6	−79.556 192	−79.570 782	−79.620 295	−79.615 555	−79.665 068	185.0	11.8
CH_3CH_2OH	−154.595 132	−154.636 321	−154.737 139	−154.686 564	−154.787 381	200.2	14.0
$CH_3CH{=}CH_2$	−117.526 219	−117.543 553	−117.616 874	−117.600 505	−117.673 826	198.6	13.4
$CH_3CH{=}CH_2^{\bullet+}$	−117.175 124	−117.189 940	−117.256 510	−117.249 029	−117.315 599	193.5	14.7
(*E*)-2-butene	−156.718 661	−156.742 567	−156.839 735	−156.816 706	−156.913 168	268.8	17.3
(*Z*)-2-butene	−156.716 349	−156.740 295	−156.837 796	−156.814 434	−156.911 935	269.2	17.4
(*Z*)-2-butene$^{\bullet+}$	−156.386 221	−156.407 565	−156.498 982	−156.484 544	−156.575 961	264.4	18.8
2-methylpropene	−156.720 637	−156.744 192	−156.842 345	−156.818 082	−156.916 235	268.7	16.8

[a] Total energies in units of hartree, 1 hartree = 2625.5 kJ mol^{-1}. [b] *E*{QCISD(T)/6-311+G(3df,2p)} = *E*{QCISD(T)/6-311G(d,p)} + *E*{MP2/6-311+G(3df,2p)} − *E*{MP2/6-311G(d,p)}. [c] In units of kJ mol^{-1}. [d] From MP2(FULL)/6-31+G(d,p) harmonic frequencies. [e] Ion energies on optimized neutral structures.

Table 2. Ab Initio Total Energies for the 2-Propenol Isomers[a]

species	MP2(FULL)/ 6-31+G(d,p)	MP2/ 6-311G(d,p)	MP2/ 6-311+G(3df,2p)	QCISD(T)/ 6-311G(d,p)	QCISD(T)/ 6-311+G(3df,2p)[b]	ZPVE[c]	$H_{298} - H_0$[c]
syn-2-propenol (**2s**)	−192.579 148	−192.625 720	−192.749 018	−192.686 651	−192.809 949	212.2	15.5
						213.4[d]	15.9[d]
anti-2-propenol (**2a**)	−192.575 398	−192.621 676	−192.746 114	−192.682 971	−192.807 408	210.9	16.4
syn-2-propenol$^{\bullet+}$ (**2s**$^{\bullet+}$)	−192.262 231	−192.310 176	−192.423 694	−192.374 058	−192.487 577	208.9	16.7
syn-2-propenol$^{\bullet+}$(N)[e] (**2s**$^{\bullet+}$(N)[e])		−192.296 599	−192.410 621	−192.361 370	−192.475 392		
anti-2-propenol$^{\bullet+}$ (**2a**$^{\bullet+}$)	−192.264 506	−192.312 182	−192.425 607	−192.375 920	−192.489 345	209.6	16.4
anti-2-propenol$^{\bullet+}$(N)[e] (**2a**$^{\bullet+}$(N)[e])		−192.298 116	−192.412 063	−192.362 858	−192.476 805		
acetone	−192.602 080	−192.647 603	−192.768 115	−192.708 521	−192.829 033	208.8	17.1
						212.4[d]	17.0[d]
acetone$^{\bullet+}$	−192.236 944	−192.286 732	−192.396 673	−192.363 150	−192.473 091	205.6	17.4

[a] Total energies in units of hartree, 1 hartree = 2625.5 kJ mol^{-1}. [b] *E*{QCISD(T)/6-311+G(3df,2p)} = *E*{QCISD(T)/6-311G(d,p)} + *E*{MP2/6-311+G(3df,2p)} − *E*{MP2/6-311G(d,p)}. [c] In units of kJ mol^{-1}. [d] From MP2(FULL)/6-31+G(d,p) harmonic frequencies. [e] Ion energies on optimized neutral structures.

calculations were carried out using the Austin Model 1[31] Solvation Model 4 with Specific Range Parameters[32,33] (AM1-SM4-SRP) self-consistent reaction field (SCRF) model. These calculations used AMSOL v. 5.0.[34]

Results and Discussion

Structures. The MP2/6-31+G(d,p) optimized structures of neutral enols **1s**, **1a** through **6s**, **6a** and their cation radicals are presented in Figures 1−6. Optimized structures of the auxiliary molecules, listed in Tables 1−4, are available as supporting information. The structure of **1s** has been studied in detail previously,[15,21] and critically evaluated bond lengths and angles are available from the work of Smith and Radom.[21] The present calculations (Figure 1) show good agreement with the "best" geometry,[21] giving 0.003 Å and 0.5° root-mean-square deviations (rmsd) for the two sets of data. The anti rotamer **1a** shows a smaller OCC angle than does **1s** whereas the bond lengths and the other bond angles are very similar. Substantial changes in geometry occur on ionization.[13,14] Ions **1s**$^{\bullet+}$ and **1a**$^{\bullet+}$ show significantly shorter C−O bonds and longer C=C bonds than do **1s** and **1a**, respectively, while the HOC angles increase and the OCC angles decrease in the cation radicals. This is consistent with an increased double bond character of the C−O

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Table 3. Ab Initio Total Energies for the 1-Propenol Isomers[a]

species	MP2(FULL)/ 6-31+G(d,p)	MP2/ 6-311G(d,p)	MP2/ 6-311+G(3df,2p)	QCISD(T)/ 6-311G(d,p)	QCISD(T)/ 6-311+G(3df,2p)[b]	ZPVE[c]	$H_{298} - H_0$[c]
syn-(*E*)-1-propenol (**3s**)	−192.572 048	−192.619 091	−192.741 601	−192.680 400	−192.802 911	212.7	16.1
anti-(*E*)-1-propenol (**3a**)	−192.569 624	−192.615 928	−192.739 595	−192.677 576	−192.801 243	210.8	17.5
syn-(*Z*)-1-propenol (**4s**)	−192.571 955	−192.619 018	−192.741 876	−192.680 324	−192.803 181	212.8	16.4
anti-(*Z*)-1-propenol (**4a**)	−192.571 199	−192.617 605	−192.741 096	−192.679 071	−192.802 561	211.8	16.9
syn-(*E*)-1-propenol$^{\bullet+}$ (**3s**$^{\bullet+}$)	−192.258 553	−192.306 919	−192.420 189	−192.371 064	−192.484 334	212.1	16.3
syn-(*E*)-1-propenol$^{\bullet+}$(N)[d] (**3s**$^{\bullet+}$(N)[d])		−192.294 865	−192.408 304	−192.360 108	−192.473 547		
anti-(*E*)-1-propenol$^{\bullet+}$ (**3a**$^{\bullet+}$)	−192.262 193	−192.310 076	−192.423 298	−192.373 940	−192.487 162	212.1	16.3
anti-(*E*)-1-propenol$^{\bullet+}$(N)[d] (**3a**$^{\bullet+}$(N)[d])		−192.297 118	−192.410 540	−192.362 312	−192.475 734		
syn-(*Z*)-1-propenol$^{\bullet+}$ (**4s**$^{\bullet+}$)	−192.257 315	−192.305 956	−192.419 432	−192.370 114	−192.483 590	212.2	16.4
syn-(*Z*)-1-propenol(N)[d] (**4s**$^{\bullet+}$(N)[d])		−192.293 778	−192.407 388	−192.359 118	−192.472 728		
anti-(*Z*)-1-propenol$^{\bullet+}$ (**4a**$^{\bullet+}$)	−192.262 693	−192.310 887	−192.423 803	−192.374 647	−192.487 563	212.7	16.2
anti-(*Z*)-1-propenol$^{\bullet+}$(N)[d] (**4a**$^{\bullet+}$(N)[d])		−192.297 904	−192.411 045	−192.363 105	−192.476 246		
propanal	−192.591 416	−192.638 711	−192.757 452	−192.699 848	−192.818 589	211.1	15.9
propanal$^{\bullet+}$	−192.212 297	−192.263 399	−192.372 255	−192.341 001	−192.449 857	206.8	16.4

[a] Total energies in units of hartree, 1 hartree = 2625.5 kJ mol^{-1}. [b] *E*{QCISD(T)/6-311+G(3df,2p)} = *E*{QCISD(T)/6-311G(d,p)} + *E*{MP2/6-311+G(3df,2p)} − *E*{MP2/6-311G(d,p)}. [c] In units of kJ mol^{-1}. [d] Ion energies on optimized neutral structures.

Table 4. Ab Initio Total Energies for the 2-Buten-2-ol Isomers[a]

species	MP2(FULL)/ 6-31+G(d,p)	MP2/ 6-311G(d,p)	MP2/ 6-311+G(3df,2p)	QCISD(T)/ 6-311G(d,p)	QCISD(T)/ 6-311+G(3df,2p)[b]	ZPVE[c]	$H_{298} - H_0$[c]
syn-(*E*)-2-buten-2-ol (**5s**)	−231.767 376	−231.820 346	−231.967 639	−231.898 752	−232.046 045	282.0	20.0
anti-(*E*)-2-buten-2-ol (**6a**)	−231.763 987	−231.816 709	−231.964 517	−231.895 512	−232.043 320	281.1	20.6
syn-(*Z*)-2-buten-2-ol (**6s**)	−231.769 130	−231.822 378	−231.969 522	−231.900 773	−232.047 917	281.8	20.4
anti-(*Z*)-2-buten-2-ol (**5a**)	−231.767 468	−231.820 292	−231.967 831	−231.898 887	−232.046 426	280.7	21.0
syn-(*E*)-2-buten-2-ol$^{\bullet+}$ (**5s**$^{\bullet+}$)	−231.468 296	−231.522 367	−231.660 758	−231.604 167	−231.742 558	280.5	20.5
syn-(*E*)-2-buten-2-ol$^{\bullet+}$(N)[d] (**5s**$^{\bullet+}$(N)[d])		−231.508 015	−231.646 858	−231.591 088	−231.729 931		
anti-(*E*)-2-buten-2-ol$^{\bullet+}$ (**5a**$^{\bullet+}$)	−231.470 379	−231.524 106	−231.662 602	−231.605 690	−231.744 186	280.8	20.4
anti-(*E*)-2-buten-2-ol$^{\bullet+}$(N)[d] (**5a**$^{\bullet+}$)		−231.505 492	−231.644 185	−231.588 913	−231.727 605		
syn-(*Z*)-2-buten-2-ol$^{\bullet+}$ (**6s**$^{\bullet+}$)	−231.467 940	−231.522 145	−231.660 537	−231.604 028	−231.742 420	279.9	21.0
syn-(*Z*)-2-buten-2-ol$^{\bullet+}$(N)[d] (**6s**$^{\bullet+}$(N)[d])		−231.509 143	−231.647 802	−231.592 241	−231.730 900		
anti-(*Z*)-2-buten-2-ol$^{\bullet+}$ (**6a**$^{\bullet+}$)	−231.471 675	−231.525 638	−231.663 757	−231.607 200	−231.745 319	280.5	20.8
anti-(*Z*)-2-buten-2-ol$^{\bullet+}$(N)[d] (**6a**$^{\bullet+}$(N)[d])		−231.509 786	−231.648 114	−231.592 936	−231.731 265		
2-butanone (eclipsed) (**7a**)	−231.791 213	−231.843 946	−231.987 600	−231.922 673	−232.066 327	280.4	20.3
2-butanone (gauche) (**7b**)	−231.789 497	−231.841 726	−231.985 922	−231.920 392	−232.064 588	281.3	19.9

[a] Total energies in units of hartree, 1 hartree = 2625.5 kJ mol^{-1}. [b] *E*{QCISD(T)/6-311+G(3df,2p)} = *E*{QCISD(T)/6-311G(d,p)} + *E*{MP2/6-311+G(3df,2p)} − *E*{MP2/6-311G(d,p)}. [c] In units of kJ mol^{-1}. [d] Ion energies on optimized neutral structures.

bond and a weakened C=C bond in **1s**$^{\bullet+}$ and **1a**$^{\bullet+}$ as discussed previously.[12a,g,14]

The optimized structures of **2s** and **2a** show very similar bond lengths and angles (Figure 2) with the exception of the O−C=C angle, which is larger in **2s**. The methyl group eclipses the C=C bond in both rotamers, which belong to the C_s symmetry group. Symmetry is broken in cation radicals **2s**$^{\bullet+}$ and **2a**$^{\bullet+}$ by methyl group rotation, which is more pronounced in the anti isomer **2a**$^{\bullet+}$ (Figure 2). The H_2C=C(O)−C skeleton of **2a**$^{\bullet+}$ shows a slight pyramidization at C_2 and C_1, whereas the H−O−C=C system is planar. The asymmetric twist of the methyl group in **2s**$^{\bullet+}$ and **2a**$^{\bullet+}$, which makes one of the C−H bond axial with respect to the C=C bond, is analogous to that in the methanol cation radical.[35] This tendency can be attributed to an increased hyperconjugation of the axial C−H σ-bond with the semioccupied π-orbital.[35,36] Other changes in bond lengths and angles in **2s**$^{\bullet+}$ and **2a**$^{\bullet+}$ as compared to **2s** and **2a**, respectively, are analogous to those obtained for the homologous vinyl alcohol system.

The optimized structures of **3s**, **3a**, **3s**$^{\bullet+}$, **3a**$^{\bullet+}$, **4s**, **4a**, **4s**$^{\bullet+}$, and **4a**$^{\bullet+}$ all show C_s symmetry with the methyl C−H bonds eclipsing the C=C bond (Figures 3 and 4).[14] Other structural features are analogous to those in **1s** and **1a**, including the changes in bond lengths and angles upon ionization. In addition, the CH_3−CH bonds are significantly shortened upon ionization due to more efficient hyperconjugation of the methyl with the semioccupied π-orbital.[35,36] It is worth noting that the closest distance between the in-plane methyl and hydroxyl hydrogen atoms, C−H···H−O, is comparable in **4s** and **4s**$^{\bullet+}$ (2.00 and 2.03 Å, respectively), indicating similar steric interactions of the hydroxyl and methyl groups in the neutral molecules and the ion.

The 2-butenols **5s**, **5a**, **6s**, and **6a** and their cation radicals represent a more complex system due to combined rotations of the C_3 and C_4 methyls and the hydroxyl group (Figures 5 and 6). The syn-*E* and syn-*Z* isomers (**5s** and **6s**, respectively) are obtained with C_s symmetry in which the in-plane C−H bonds of both methyl groups eclipse the C=C bonds (Figure 5 and 6). By contrast, the anti isomers **5a** and **6a** show significant

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Table 5. Relative Enthalpies, Entropies, and Free Energies of Syn and Anti Enol Rotamers[a]

enol	T, K	$\Delta H_{r,0}$	$\Delta H^\circ_{r,T}$	$\Delta S^\circ_{r,T}$	$\Delta G^\circ_{r,T}$	% isomer[b]
1s → **1a**	298	3.5	4.2	5.8	2.5	73
	298		4.2[c]	5.2[c]	2.6[c]	74
	400		4.3	6.2	1.8	63
	400		4.1[c]	5.1[c]	2.1[c]	65
2s → **2a**	298	5.4	6.2	7.6	4.0	83
	400		6.4	7.9	3.2	73
3s → **3a**	298	2.5	3.9	8.4	1.4	63
	400		4.0	7.6	1.0	57
4s → **4a**	298	0.67	1.25	5.9	−0.5	55
	400		1.35	6.3	−1.2	59
5s → **5a**	298	6.2	6.7	3.8	5.6	93
	400		6.8	4.1	5.2	88
6s → **6a**	298	2.8	3.5	0.7	3.3	79
	400		3.6	1.0	3.2	73
1s$^{\bullet+}$ → **1a**$^{\bullet+}$	298	−7.4	−7.5	−0.8	−7.2	95
	400		−7.5	−0.9	−7.2	90
2s$^{\bullet+}$ → **2a**$^{\bullet+}$	298	−4.0	−4.2	−0.9	−4.0	83
	400		−4.5	−1.1	−4.1	77
3s$^{\bullet+}$ → **3a**$^{\bullet+}$	298	−7.3	−7.4	−1.3	−7.0	94
	400		−7.4	−1.3	−6.9	89
4s$^{\bullet+}$ → **4a**$^{\bullet+}$	298	−10.0	−10.2	−6.9	−8.1	96
	400		−10.1	−7.1	−7.4	90
5s$^{\bullet+}$ → **5a**$^{\bullet+}$	298	−3.9	−4.0	−1.7	−3.5	81
	400		−4.0	−1.7	−3.4	73
6s$^{\bullet+}$ → **6a**$^{\bullet+}$	298	−7.0	−7.2	−3.7	−6.1	92
	400		−7.2	−3.8	−5.7	85

[a] From QCISD(T)/6-311+G(3df,2p) relative energies (eq 1, Tables 1−4), HF/6-31+G(d,p) zero-point energies and $H_T - H_0$ enthalpy corrections; enthalpies in kJ mol^{-1}, entropies in J mol^{-1} K^{-1}. [b] Thermodynamically more stable rotamer. [c] C−OH torsion treated as a hindered rotation.

out-of-plane rotation of the hydroxyl group, which is more pronounced in **5a** (Figure 5). Rotation of the hydroxyl group is combined with opening of the OC_1C_3 angle in **5a** and **6a** and with rotation of the C_3 methyl group in **6a**. The cation radicals show a different behavior. **5s**$^{\bullet+}$ and **5a**$^{\bullet+}$ are obtained with C_s symmetry in which the C_3 methyls are rotated to eclipse the C_1−O bonds (Figure 5). In contrast to **6a**, ion **6a**$^{\bullet+}$ is obtained with C_s symmetry with the C−H bonds of both methyl groups eclipsing the C═C bond. Finally, **6s**$^{\bullet+}$ shows a substantial twist of the C_3 methyl group causing one of the C_3−H bonds to be perpendicular with respect to the C═C−C_3 plane (Figure 6).

Syn−Anti and *E*−*Z* Isomers. The enthalpy differences, calculated at the approximated QCISD(T)/6-311+G(3df,2p) level and including zero-point corrections, for the rotamers of vinyl alcohol, 2-propenol, 1-propenols, and 2-butenols show that the syn isomers are generally more stable in the neutral enols, while the anti isomers are more stable for the cation radicals (Table 5). This finding is in qualitative agreement with the previous ab initio studies of enols[12,14] and enol cation radicals.[13] The methyl substituents at the enol double bond have an effect on the relative stabilities of the syn and anti isomers. With neutral enols, an α-methyl substituent stabilizes the syn isomer whereas a *Z*-*β*-methyl substituent destabilizes it (Table 5); these effects are presumably entirely steric in origin. The effect of an *E*-*β*-methyl substituent is weak and ambiguous. Weak syn stabilization is found for **5s**, **5a** compared with **2s**, **2a**, while syn destabilization follows for **3s**, **3a** compared with **1s**, **1a**. The syn−anti relative enthalpies from the present G2(MP2) calculations (Table 5) are notably lower than those reported by Apeloig and co-workers based on their Hartree−Fock level calculations, e.g., 7.9, 4.6, 12.6, and 5.4 kJ mol^{-1} for **3s** → **3a**, **4s** → **4a**, **5s** → **5a**, and **6s** → **6a**, respectively.[12c] However, the trends in these two sets of data are similar.

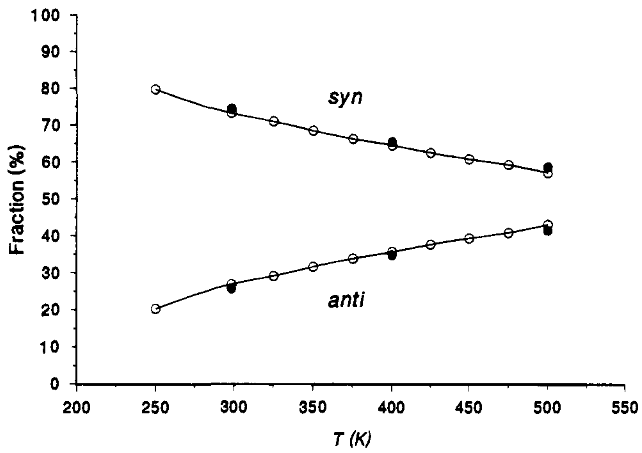

Figure 7. Equilibrium populations of **1s** and **1a** in the gas phase: (○) RRHO calculations; (●) calculations including C−OH hindered rotation.

The general preference for the anti geometry in the enol cation radicals is also affected by methyl substituents (Table 5). α-Methyl substituents destabilize the anti isomers by 3−4 kJ mol^{-1}, while *Z*-*β*-methyl substituents stabilize the anti isomers by ~3 kJ mol^{-1}. The effect of an *E*-*β*-methyl substituent is negligible, *viz.*, **1s**$^{\bullet+}$, **1a**$^{\bullet+}$ compared with **3s**$^{\bullet+}$,**3a**$^{\bullet+}$ (Table 5).

The thermodynamics of neutral enols and enol cation radicals is important for predicting the equilibrium populations of the syn and anti rotamers produced in the gas phase at various experimental temperatures.[9,10,15,17] Table 5 summarizes the calculated relative enthalpies ($\Delta H^\circ_{r,T}$), entropies ($\Delta S^\circ_{r,T}$), and free energies ($\Delta G^\circ_{r,T}$). Before discussing the calculated equilibria, we address the question of the adequacy of the RRHO model for enol molecules. Enols **1**−**6** have low-frequency vibrational modes due to hydroxyl and/or methyl torsions. These can be treated as vibrations (as in the RRHO model), hindered rotations,[28] or free rotations,[37] which results in contributions to H°_T and S°_T decreasing in the same order for the wavenumbers in question. For the rotamers of **2** and **3**, the methyl torsional modes have very similar low wavenumbers, e.g., 181, 199, 190, and 197 cm^{-1} for **2s**, **2a**, **3s**, and **3a**, respectively, and so treating those as vibrations or free rotations results in very similar $\Delta H^\circ_{r,T}$ and $\Delta S^\circ_{r,T}$ values, for the corresponding terms largely cancel out. By contrast, the wavenumbers for the hydroxyl torsion in rotamers differ, e.g., 390, 176, 382, 106, 369, and 15 cm^{-1} for **1s**, **1a**, **2s**, **2a**, **3s**, and **3a**, respectively. The torsions in **1s**, **1a**, **2s**, **2a**, and **3s** were treated as vibrations. The torsional frequency in **3a** (15 cm^{-1}) is too small to be compatible with a harmonic frequency approximation at 298 K, and it also implies a very low barrier for the **3a** → **3s** isomerization.[37] Hence the latter mode was considered a free internal rotation. The situation is further complicated in **4**−**6**, in which the methyl and hydroxyl torsions are coupled, making the free-rotor approximation invalid unless at high temperatures. However, the softest torsions have similar wavenumbers, e.g., 64 and 87 cm^{-1}, for **4s** and **4a**, respectively, and so their contributions will largely cancel out in the calculated $\Delta H^\circ_{r,T}$ and $\Delta S^\circ_{r,T}$, regardless of whether those modes are treated as vibrations or free rotations. To analyze the adequacy of the RRHO model, the $\Delta H^\circ_{r,T}$ and $\Delta S^\circ_{r,T}$ values obtained with it were compared with those calculated using Pitzer's scheme for hindered rotation[28] in **1s** and **1a**. The potential energy barrier for **1s** → **1a** was calculated as 21.3 kJ mol^{-1} with MP2(FULL)/6-31+G(d,p). Table 5 shows that both approaches give nearly identical $\Delta H^\circ_{r,T}$ and similar $\Delta S^\circ_{r,T}$ values in the 298−400 K temperature range. Hence, considering hindered rotations has only a small effect on the relative free energies and the corresponding equilibrium populations of **1s** and **1a** (Figure 7).

A similar conclusion concerning hindered rotation in CH_2OH was recently reached by Bauschlicher and Partridge.[38]

The data in Table 5 show that, in general, the thermochemically more stable rotamers are more populated in the gas phase at 298−400 K. (*Z*)-1-Propenols are an exception as the thermochemically more stable **4s** is *less* populated at or above ca. 230 K due to the positive $\Delta S°_{r,T}$ for rotamer equilibration. Experimental measurements of syn−anti isomer populations relevant to simple enols are scarce.[39] Owen and Sheppard detected the syn and anti rotamers of methyl vinyl ether in the gas phase and deduced $\Delta H°_{r,298} = 4.8$ kJ mol^{-1} favoring the syn isomer.[40] Our calculated enthalpy difference for vinyl alcohol (4.2 kJ mol^{-1}, Table 5) is close to the value for vinyl methyl ether. Capon and Siddhanta studied the ^{1}H-NMR spectra of 1-propenols in aqueous acetone solution at 193 K and found that both the *E* and *Z* isomers existed as mixtures of rotamers.[41] For **3** a higher proportion of **3s** was deduced, while **4** was found to contain more **4a**, and the fractions of the more abundant isomers were found to decrease with increasing temperature.[41] The calculated $\Delta G°_{r,T}$ for the gas-phase equilibria are consistent with the observed populations of **3s** and **3a** and **4s** and **4a** in solution.[41] However, the **4s** $\rightleftharpoons$ **4a** equilibrium is dominated by entropy effects which should cause the fraction of **4a** to slightly increase with temperature in contrast to the trend observed in solution. One might note that solution equilibria in polar solvents are affected by electrostatic interactions[5e,12e] that should to first order favor the anti isomers since they have greater dipole moments.[42] This is in accord with dielectric continuum solvation calculations for **1** and **2** (vide infra). The qualitative disagreement between theory and experiment regarding the temperature dependence is likely to be due to entropy differences associated with the first solvation shells about **4a** and **4s**; such subtle effects are difficult to calculate and are not addressed in this work.

The thermodynamic data for the enol cation radicals indicate that the more stable anti isomer should predominate in the gas phase. This is especially true for enol ions formed by unimolecular dissociations at threshold energies,[8] which should yield anti isomers of 80−95% purity (Table 5).

The relative 298 K enthalpies for the *E* and *Z* enols show the Z isomers to be more stable. The corresponding $\Delta\Delta H°_{f,298}$ values for $Z \rightarrow E$ are small for **4s** → **3s** and **4a**$^{•+}$ → **3a**$^{•+}$, giving 0.3 and 0.6 kJ mol^{-1}, respectively. Isomer relative stabilities are more pronounced with **6s** → **5s** ($\Delta\Delta H°_{f,298} = 4.9$ kJ mol^{-1}), possibly due to a combination of a stabilizing cis $OH\cdots CH_3$ interaction in **6s** and a destabilizing cis $CH_3\cdots CH_3$ interaction in **5s**. By comparison, (*Z*)-2-butene is calculated to be 3.7 kJ mol^{-1} less stable than (*E*)-2-butene; the experimental $\Delta\Delta H°_{f,298}$ value for the latter system is 4.4 kJ mol^{-1},[44] in good agreement with the calculated value. In the ionic system, **6a**$^{•+}$ → **5a**$^{•+}$ gives $\Delta\Delta H°_{f,298} = 2.9$ kJ mol^{-1} preferring the *Z* isomer.

Thermochemistry of Neutral Enols. Standard enthalpies of formation for the enols and enol cation radicals were obtained from the calculated enthalpies of isodesmic reactions, eq 2 and 3, and standard thermochemical data.[44]

$$R_2{-}CH{=}C(OH){-}R_1 + CH_4 \rightarrow R_2{-}CH{=}CH{-}R_1 + CH_3OH \quad (2)$$

$$R_2{-}CH{=}C(OH){-}R_1 + C_2H_6 \rightarrow R_2{-}CH{=}CH{-}R_1 + CH_3CH_2OH \quad (3)$$

The enol relative enthalpies were further interrelated via isodesmic reactions 4−7.

$$R_2{-}CH{=}CH{-}OH + C_2H_6 \rightarrow R_2{-}CH{=}C(OH){-}CH_3 + CH_4 \quad (4)$$

$$R_2{-}CH{=}CH{-}OH + CH_3CH{=}CH_2 \rightarrow R_2{-}CH{=}C(OH){-}CH_3 + C_2H_4 \quad (5)$$

$$CH_2{=}C(OH){-}R_1 + C_2H_6 \rightarrow CH_3{-}CH{=}C(OH){-}R_1 + CH_4 \quad (6)$$

$$CH_2{=}C(OH){-}R_1 + CH_3CH{=}CH_2 \rightarrow CH_3{-}CH{=}C(OH){-}R_1 + C_2H_4 \quad (7)$$

G2(MP2) calculations in general give accurate enthalpies for isodesmic reactions with the exception of those involving CO_2 and SO_2 for which the agreement has been less satisfactory.[20,45] As an internal test of the present set we calculated the enthalpies of 25 isodesmic reactions for methyl transfer among methane, ethane, ethylene, propene, (*E*)-2-butene, methanol, ethanol, acetaldehyde, propanal, acetone, and 2-butanone. The root-mean-square deviation (rmsd) of the calculated and experimental enthalpies was 1.3 kJ mol^{-1}, which barely exceeded the rmsd from the uncertainties in the experimental data alone (1.2 kJ mol^{-1}).[44] Hence the G2(MP2) scheme was deemed to provide relative enthalpies of acceptable quality.

The enthalpies of isodesmic reactions (eq 2−7) for neutral enols and the ensuing standard enthalpies of formation are summarized in Table 6. The $\Delta H°_{f,298}$(**1s**) from the enthalpies of two isodesmic reactions agree within 0.4 kJ mol^{-1}. By comparison, the calculated enthalpy of tautomerization to acetaldehyde appears to be too high by 3.9 kJ mol^{-1}. This difference is diminished to 2.3 kJ mol^{-1} when MP2 harmonic frequencies are used to evaluate the zero-point and enthalpy corrections in **1s** and acetaldehyde. The G2(MP2) enthalpy of isomerization is similar to that obtained by Radom and co-workers from their G1 calculations.[16] The other ΔH(enol−oxo) values reported previously depended on the size of the basis set and the post-Hartree−Fock treatment of the correlation energy.[12e,14] With improvements in both, the ΔH(enol−oxo) values show a decreasing trend, e.g., −70 kJ mol^{-1} for MP4/6-31G(d,p),[12e] −54 kJ mol^{-1} for MP4/6-311+G(d,p),[12d] to −44 kJ mol^{-1} in the present highest-level calculations. Effects of the basis set on the calculated ΔH(enol−oxo) have been noted

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(42) The HF/6-31+G(d,p) calculated dipole moments of the enols, scaled by 0.73, were (in debye): 0.9 (**1s**), 1.8 (**1a**), 0.5 (**2s**), 2.1 (**2a**), 1.2 (**3s**), 1.6 (**3a**), 1.3 (**4s**), and 1.5 (**4a**). The scaling factor was chosen to fit the calculated and experimental dipole moments of acetaldehyde (2.69 D) and acetone (2.88 D) from ref 43.

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Table 6. Relative Enthalpies of Neutral Enols[a]

enol	$\Delta H_{r,0}$	$\Delta H^\circ_{r,298}$	$\Delta H^\circ_{f,298}$	exp[b]
1s + $CH_4 \rightarrow CH_2{=}CH_2$ + CH_3OH	49.6	49.2	−124	
1s + $C_2H_6 \rightarrow CH_2{=}CH_2$ + C_2H_5OH	24.9	25.4	−124	
1s $\rightarrow CH_3CHO$	−46.4	−45.7	−120	
	−44.6[c]	−44.1[c]	−122[c]	
1			***−123***	−125 −128[d]
2s + $CH_4 \rightarrow CH_3CH{=}CH_2$ + CH_3OH	62.6	61.8	−169	
2s + $C_2H_6 \rightarrow CH_3CH{=}CH_2$ + C_2H_5OH	37.9	38.0	−168	
2s + $CH_4 \rightarrow$ **1s** + C_2H_6	32.4	36.7	−168	
2s + $CH_2{=}CH_2 \rightarrow$ **1s** + $CH_3CH{=}CH_2$	11.8	13.0	−168	
2s + $CH_3CH{=}CH_2 \rightarrow$ **1s** + $(CH_3)_2C{=}CH_2$	7.3	7.4	−167	
2s $\rightarrow CH_3COCH_3$	−53.5	−51.9	−165	
	−51.1[c]	−50.0[c]	−167[c]	
2			***−167***	−170[d]
3s + $CH_4 \rightarrow CH_3CH{=}CH_2$ + CH_3OH	43.6	42.2	−149	
3s + $C_2H_6 \rightarrow CH_3CH{=}CH_2$ + C_2H_5OH	18.9	18.4	−149	
3s + $CH_4 \rightarrow$ **1s** + C_2H_6	17.7	15.6	−148	
3s + $CH_2{=}CH_2 \rightarrow$ **1s** + $CH_3CH{=}CH_2$	−6.0	−7.0	−148	
3s $\rightarrow CH_3CH_2CHO$	−42.8	−43.0	−144	
3			***−147***	−169
4s + $CH_4 \rightarrow CH_3CH{=}CH_2$ + CH_3OH	44.2	42.5	−150	
4s + $C_2H_6 \rightarrow CH_3CH{=}CH_2$ + C_2H_5OH	19.5	18.7	−149	
4s + $CH_4 \rightarrow$ **1s** + C_2H_6	18.3	15.9	−149	
4s + $CH_2{=}CH_2 \rightarrow$ **1s** + $CH_3CH{=}CH_2$	−5.4	−6.7	−149	
4s $\rightarrow CH_3CH_2CHO$	−42.8	−43.0	−145	
4			***−148***	−174
5s + $CH_4 \rightarrow$ (*Z*)-2-butene + CH_3OH	58.1	56.8	−192	
5s + $C_2H_6 \rightarrow$ (*Z*)-2-butene + C_2H_5OH	33.4	33.0	−192	
5s + $CH_2{=}CH_2 \rightarrow$ **1s** + (Z)-2-butene	8.5	7.6	−192	
5s + $CH_2{=}CH_2 \rightarrow$ **2s** + $CH_3CH{=}CH_2$	−10.5	−12.1	−188	
5s $\rightarrow CH_3COCH_2CH_3$	−54.3	−54.0	−187	
5			***−190***	−212[d]
6s + $CH_4 \rightarrow$ (*E*)-2-butene + CH_3OH	59.6	57.8	−197	
6s + $C_2H_6 \rightarrow$ (*E*)-2-butene + C_2H_5OH	34.9	34.0	−197	
6s + $CH_2{=}CH_2 \rightarrow$ **1s** + (E)-2-butene	10.0	8.6	−197	
6s + $CH_2{=}CH_2 \rightarrow$ **2s** + $CH_3CH{=}CH_2$	−5.4	−7.4	−193	
6s $\rightarrow CH_3COCH_2CH_3$	−49.2	−49.3	−191	
6			***−195***	−214[d]

[a] In kJ mol^{-1}. [b] From ref 44b. [c] MP2(FULL)/6-31+G(d,p) zero-point energies and enthalpy corrections. [d] From ref 8b.

previously.[12e] The $\Delta H^\circ_{f,298}$ for **1** is obtained as −123 kJ mol^{-1} by averaging the enthalpies of formation of **1s** and **1a** over the isomer equilibrium populations (Table 5). The calculated $\Delta H^\circ_{f,298}$ of **1** is only slightly higher than the previous experimental estimates, −128[8b] and −125 kJ mol^{-1}.[44]

The isodesmic reactions for the acetone enol **2s** give consistent results when based on hydroxyl exchange with methane and ethane, or methyl exchange with **1s**. The enthalpy of isomerization to acetone is overestimated by 2.9 kJ mol^{-1} resulting in a somewhat higher $\Delta H^\circ_{f,298}$ for the enol. However, the difference decreases to a mere 1 kJ mol^{-1} when MP2 zero-point and enthalpy corrections[38] are employed (Table 6). The ΔH(enol−oxo) values diminish with the increasing size of the basis set, e.g., −77, −59, and −52 kJ mol^{-1} for MP2 calculations with the 6-31G(d),[12e] 6-311G(d,p), and 6-311+G-(3df,2p) basis sets, respectively. After averaging the equilibrium contributions of **2s** and **2a**, the $\Delta H^\circ_{f,298}$ of **2** is obtained as −167 kJ mol^{-1} (Table 6). This value is in an excellent, although perhaps fortuitous, agreement with the experimental estimate,[8b] whereas a recent compendium of thermochemical data reports −176 kJ mol^{-1} for $\Delta H_{f,298}$(**2**).[44] In order to check the calculated $\Delta H^\circ_{f,298}$(**2**) we added another isodesmic reaction for methyl exchange between **2s** and propene, such that both sides of the reaction would contain a quaternary sp^2 carbon atom (Table 6). However, the resulting $\Delta H^\circ_{f,298}$ is within 1 kJ mol^{-1} of the mean of the other determinations (Table 6), attesting to the consistency of the calculated values.

The $\Delta H^\circ_{f,298}$ of enols **3** and **4** are obtained from four isodesmic reactions (Table 6) and averaged over the rotamer populations. The values $\Delta H^\circ_{f,298}$(**3**) = −147 kJ mol^{-1} and $\Delta H^\circ_{f,298}$(**4**) = −148 kJ mol^{-1} are substantially higher than the experimental estimates.[8b,44,46] We attribute these differences to the experimental enthalpies of formation of cation radicals $\mathbf{3}^{\bullet+}$ and $\mathbf{4}^{\bullet+}$, which are perhaps too low, as discussed below. Tautomerization of **3** and **4** to propanal gives $\Delta H^\circ_{f,298}$ for the enols that are 4.3 kJ mol^{-1} higher than those from isodesmic reactions (Table 6). No previous post-Hartree−Fock calculations of ΔH(enol−oxo) have been reported for **3s**, **3a**, **4s**, and **4a**. The present data show dependence on the size of the basis set, e.g., ΔH(enol−oxo) = −53 and −43 kJ mol^{-1} for MP2 calculations with the 6-311G(d,p) and 6-311+G(3df,2p) basis set, respectively. The QCISD(T) procedure has only a small effect on the final ΔH(enol−oxo) value.

Isodesmic reactions of **5s** with methane, ethane, and ethylene give $\Delta H^\circ_{f,298}$ values within 4 kJ mol^{-1} (Table 6), and a similar level of consistency is obtained for **6s**. The enthalpies of tautomerizations to 2-butanone yield somewhat higher enthalpies of formation for **5s** and **6s** in line with the results from tautomerizations of the other enols. The population-averaged enthalpies of formation, based on the isodesmic reactions, are $\Delta H^\circ_{f,298}$(**5**) = −190 kJ mol^{-1} and $\Delta H^\circ_{f,298}$(**6**) = −195 kJ mol^{-1}. As for **3** and **4**, the calculated enthalpies of formation for **5** and **6** are substantially higher than the experimental estimates that were based on ion enthalpies of formation and threshold ionization energies.[8b]

The calculated $\Delta H^\circ_{f,298}$ of enols are compared with the estimates obtained from empirical schemes put forth by Turecek, Brabec, and Korvola (TBK),[8b] Keeffe and Kresge (KK),[7] and Guthrie (JPG).[39b] The TBK scheme was based on the gas-phase data from electron impact measurements, which were used to calculate the O−(H)(C$_d$) group equivalent for the Benson additivity scheme.[47] The KK and JPG schemes combined solution ΔG° data from equilibrium measurements with estimated entropy corrections, enthalpies of hydrogenation, and evaporation to arrive at enol enthalpies of formation in the gas phase.[7,39b] The enthalpies of formation of **1**−**6** (Table 6) yield the O−(H)(C$_d$) group equivalent in the −195 to −178 kJ mol^{-1} range. Although the average value (−183 kJ mol^{-1}) is notably lower than that from electron impact measurements (−202 kJ mol^{-1})[8b,46] the two sets of data give similar standard deviations, 6.6 and 6 kJ mol^{-1}, respectively. The calculation-based term is probably more accurate as an average value; however, its application to individual enol systems is likely to give rise to

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deviations. Guthrie discussed the adequacy of Benson's scheme for enols and enol ethers and pointed out the inherent approximations and potential discrepancies, namely, the use of the $C_d-(H)(C)$ and $C_d-(C)_2$ terms instead of $C_d-(H)(O)$ and $C_d-(C)(O)$, respectively.[39b]

Comparison of the calculated ΔG(enol−oxo) values pertaining to the gas phase with those from equilibrium measurements in aqueous solution[5−7,39b] gives the following values: $\Delta G^\circ_{298}(\mathbf{1}\rightarrow CH_3CHO) = -45$ kJ mol^{-1} (-36 kJ mol^{-1} in water),[7,39b] and $\Delta G^\circ_{298}(\mathbf{2}\rightarrow \text{acetone}) = -57$ kJ mol^{-1} (-48 kJ mol^{-1} in water).[7,39b] Hence, stabilization of simple enols in water is indicated.[12e] To account for the latter effect free energies of solvation (ΔG_s) for the enols and their oxo isomers must be known. To this end we have carried out continuum dielectric calculations using the Austin Model 1[31] Solvation Model 4 with Specific Range Parameters[32,33] (AM1-SM4-SRP) self-consistent reaction field (SCRF) model for aqueous solvation. This model was specifically developed to handle hydrocarbon, oxo, and alcohol functionalities; it is parametrized to account for both electrostatic and specific first-solvation-shell effects at 298 K. The differential, Boltzmann-averaged, free energies of solvation, ΔG_s, favor the enol tautomers over the oxo by -12.5 and -5.0 kJ mol^{-1} for **1** and **2**, respectively. These theoretical corrections leave a difference in the calculated and experimental free energies in solution of -3 and 4 kJ mol^{-1} for **1** and **2**, respectively, which is a very reasonable quantitative agreement. The quantum-mechanical SCRF results may be compared to a set of empirical estimates made by Apeloig and co-workers,[12e] based on the experimental data of Abraham et al.[48] In particular, they estimate corrections of -7.3 and -4.9 kJ mol^{-1} for **1** and **2**, respectively. In the former case, the SCRF and empirical corrections differ by 5.2 kJ mol^{-1} but bracket the experimental result. In the latter case they agree closely, lending further confidence to the analysis.

Thermochemistry of Enol Cation Radicals. The enthalpies of formation of the cation radicals are obtained from isodesmic reactions

$$R_2-CH{=}C(OH)-R_1^{\bullet+} + CH_4 \rightarrow R_2-CH{=}CH-R_1^{\bullet+} + CH_3OH \quad (8)$$

$$R_2-CH{=}C(OH)-R_1^{\bullet+} + C_2H_6 \rightarrow R_2-CH{=}CH-R_1^{\bullet+} + CH_3CH_2OH \quad (9)$$

and charge-exchange (isogyric) reactions with ethylene, propene, and (*Z*)-2-butene

$$R_2-CH{=}C(OH)-R_1^{\bullet+} + R_1CH{=}CHCH_3 \rightarrow R_2-CH{=}C(OH)-R_1 + R_1CH{=}CHR_2^{\bullet+} \quad (10)$$

The enthalpies of isodesmic and isogyric reactions were also examined for 21 combinations of the auxiliary molecules and ions (Table 1). The rmsd value from the G2(MP2) calculations, 5.1 kJ mol^{-1}, is slightly higher than that based on the estimated uncertainties of the tabulated $\Delta H_{f,298}$ values (rmsd = 4.2 kJ mol^{-1}).[49] The enthalpies of isodesmic reactions for enol cation radicals and the corresponding standard enthalpies of formation are summarized in Table 7. The latter values have been calculated assuming the stationary electron convention.[44a]

Table 7. Relative Enthalpies of Enol Cation Radicals[a]

enol	$\Delta H_{r,0}$	$\Delta H^\circ_{r,298}$	$\Delta H^\circ_{f,298}$	exp[b]
1a$^{\bullet+}$ + $CH_4 \rightarrow CH_2{=}CH_2^{\bullet+}$ + CH_3OH	176.4	176.9	763	
1a$^{\bullet+}$ + $C_2H_6 \rightarrow CH_2{=}CH_2^{\bullet+}$ + C_2H_5OH	151.6	153.0	763	
1a$^{\bullet+} \rightarrow CH_3CHO$	55.0 54.8[c]	56.0 55.3[c]	765 766[c]	
1a$^{\bullet+}$ + alkene → **1a** + alkene$^{\bullet+}$			764[d]	
1a$^{\bullet+}$			765	
1$^{\bullet+}$			765	757 765[e]
2a$^{\bullet+}$ + $CH_4 \rightarrow CH_3CH{=}CH_2^{\bullet+}$ + CH_3OH	158.9	158.5	673	
2a$^{\bullet+}$ + $C_2H_6 \rightarrow CH_3CH{=}CH_2^{\bullet+}$ + C_2H_5OH	134.1	134.6	674	
2a$^{\bullet+} \rightarrow CH_3COCH_3^{\bullet+}$	38.7	39.7	679	
2a$^{\bullet+}$ + alkene → **2a** + alkene$^{\bullet+}$			679[d]	
2a$^{\bullet+}$			676	
2$^{\bullet+}$			677	658
3a$^{\bullet+}$ + $CH_4 \rightarrow CH_3CH{=}CH_2^{\bullet+}$ + CH_3OH	150.7	150.4	681	
3a$^{\bullet+}$ + $C_2H_6 \rightarrow CH_3CH{=}CH_2^{\bullet+}$ + C_2H_5OH	125.9	126.5	682	
3a$^{\bullet+} \rightarrow CH_3CH_2CHO^{\bullet+}$	92.6	92.7	681	
3a$^{\bullet+}$ + alkene → **3a** + alkene$^{\bullet+}$			683[d]	
3a$^{\bullet+}$			682	
3$^{\bullet+}$			682	666
4a$^{\bullet+}$			682	
4$^{\bullet+}$			682	664
5a$^{\bullet+}$ + $CH_4 \rightarrow$ (*Z*)-$CH_3CH{=}CHCH_3^{\bullet+}$ + CH_3OH	144.0	143.7	600	
5a$^{\bullet+}$ + $C_2H_6 \rightarrow$ (*Z*)-$CH_3CH{=}CHCH_3^{\bullet+}$ + C_2H_5OH	119.2	119.8	601	
5a$^{\bullet+}$ + alkene → **5a** + alkene$^{\bullet+}$			603[d]	
5a$^{\bullet+}$			602	
5$^{\bullet+}$			603 601[g]	582[f]
6a$^{\bullet+}$			600	
6$^{\bullet+}$			601	582[f] 601[g]

[a] In kJ mol^{-1}. [b] From ref 44b. [c] From MP2(FULL)/6-31+G(d,p) harmonic frequencies. [d] Mean value from isogyric reactions with ethylene, propene and (*Z*)-2-butene. [e] From ref 50. [f] From ref 8a. [g] From ref 8b.

Isodesmic reactions of **1a**$^{\bullet+}$ with methane and ethane, isogyric reaction with alkenes, and isomerization to acetaldehyde$^{\bullet+}$ agree on $\Delta H_{f,298}(\mathbf{1a}^{\bullet+})$ to within 1.5 kJ mol^{-1} rmsd. The $\Delta H^\circ_{f,298}(\mathbf{1}^{\bullet+})$ is calculated as 765 kJ mol^{-1} by averaging the contributions of **1a**$^{\bullet+}$ and **1s**$^{\bullet+}$ by their equilibrium populations (Table 5). The calculated value is in excellent agreement with that from a recent photoionization study of **1**$^{\bullet+}$ (765 kJ mol^{-1}),[50] and in acceptable agreement with the tabulated value (757 kJ mol^{-1}).[44b]

The calculated enthalpies of isodesmic reactions of **2a**$^{\bullet+}$ are somewhat lower than those for isogyric reactions with **1a** and ethylene, propene, or (*Z*)-2-butene, and isomerization to acetone$^{\bullet+}$. The combined reactions give an average $\Delta H^\circ_{f,298}(\mathbf{2}^{\bullet+})$

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(48) Abraham, M. H.; Whiting, G. S.; Fuchs, R.; Chambers, E. S. *J. Chem. Soc., Perkin Trans. 2* **1990**, 291.

(49) Error limits for the $\Delta H_{f,298}$ of neutral molecules were taken from ref 44b. Error limits for ionic $\Delta H_{f,298}$ were estimated as 2 kJ mol^{-1} (0.02 eV) for species with well-defined adiabatic ionization energies (ethylene, acetaldehyde, acetone), and 3 kJ mol^{-1} (0.03 eV) for species whose adiabatic ionization energies had been estimated as onsets in the photoelectron spectra (ref 44).

(50) Bouchoux, G.; Alcaraz, C.; Dutuit, O.; Nguyen, M. T. *Int. J. Mass Spectrom. Ion Processes* **1994**, *137*, 93.

(51) Holmes, J. L.; Lossing, F. P.; Burgers, P. C. *Int. J. Mass Spectrom. Ion Processes* **1983**, *47*, 133.

= 677 kJ mol^{-1}, which is adjusted for the contributions of $\mathbf{2a}^{\bullet+}$ and $\mathbf{2s}^{\bullet+}$ (Table 5). The calculated $\Delta H^\circ_{f,298}(\mathbf{2a}^{\bullet+})$ is to be compared with the experimental ΔH_f, which was obtained from appearance measurements that presumably yielded the more stable rotamer $\mathbf{2a}^{\bullet+}$. The ab initio based values are systematically higher than a recent estimate[44b] by 15−19 kJ mol^{-1}.

The discrepancy between the experimental estimate and the present value of $\Delta H^\circ_{f,298}(\mathbf{2a}^{\bullet+})$ deserves some comment. Holmes and Lossing reported $\Delta H_f(\mathbf{2}^{\bullet+})$ as 661 kJ mol^{-1} based on three appearance energy measurements.[8a] Traeger and McLoughlin discussed in detail the thermochemical treatment of the appearance energies and suggested eq 11 to correct for the non-standard temperature of the neutral (B) and ionic products (A$^+$) formed from a thermal precursor (AB) at the dissociation threshold.[18]

$$\Delta H^\circ_{f,298}(\mathrm{A}^+) = AE(\mathrm{exp}) - \Delta H^\circ_{f,298}(\mathrm{B}) + \Delta H^\circ_{f,298}(\mathrm{AB}) + \Delta H_{298}(\mathrm{A}^+) + \Delta H_{298}(\mathrm{B}) - {}^5/_2RT \quad (11)$$

AE is the measured appearance energy, and $\Delta H_{298}(\mathrm{A}^+)$ and $\Delta H_{298}(\mathrm{B})$ are the 298 K enthalpies of the products. The enthalpy corrections in eq 11 hold rigorously if the products are formed at 0 K, that is, all the available internal energy in $\mathrm{AB}^{\bullet+}$ was used for dissociation.[18] In reality, the thermal content of the products is unknown and hence the ΔH_{298} corrections represent upper limits only. Using the calculated ΔH_{298} values for $\mathbf{2a}^{\bullet+}$ as A$^+$ (Table 2) and ethylene or propene as B (Table 1),[8a] one obtains an upper limit for the $\Delta H^\circ_{f,298}(\mathbf{2}^{\bullet+})$ from the Holmes–Lossing measurements as 684 kJ mol^{-1}, which slightly exceeds the calculated value.

A discrepancy is also found between the calculated and experimental enthalpies of formation of 1-propenol cation radicals $\mathbf{3}^{\bullet+}$ and $\mathbf{4}^{\bullet+}$. The calculations based on the isodesmic and isogyric reactions, as well as isomerization to propanal$^{\bullet+}$, give consistent $\Delta H^\circ_{f,298}$ values for $\mathbf{3a}^{\bullet+}$, which, however, are 16−18 kJ mol^{-1} higher than the experimental estimate (Table 7). A similar situation is encountered with $\mathbf{4a}^{\bullet+}$ (Table 7). It should be noted that the *E* and *Z* isomers were not distinguished in the appearance energy measurements that provided the enthalpies of formation of $\mathbf{3}^{\bullet+}$ and $\mathbf{4}^{\bullet+}$.[8a] The calculations show very similar population-averaged enthalpies of formation for $\mathbf{3}^{\bullet+}$ and $\mathbf{4}^{\bullet+}$, with the latter being more stable by a mere 0.5 kJ mol^{-1} (Table 7). The differences between the experimental data and the present calculations largely disappear when enthalpy corrections to 298 K (Tables 1 and 3) are applied to the products of unimolecular dissociations used in the threshold measurements, e.g., $\mathbf{3a}^{\bullet+}$, ethylene, and propene.[8a] The 298 K corrected $\Delta H_f(\mathbf{3a}^{\bullet+})$ = 688 kJ mol^{-1} is in good agreement with the calculated data.

Isodesmic and isogyric reactions of butenol ions $\mathbf{5a}^{\bullet+}$ and $\mathbf{6a}^{\bullet+}$ give very similar $\Delta H^\circ_{f,298}$ values for the isomers. The population-averaged $\Delta H^\circ_{f,298}$ of $\mathbf{5}^{\bullet+}$ is 2.3 kJ mol^{-1} higher than that of $\mathbf{6}^{\bullet+}$, indicating that the *Z* isomer is more stable. The calculated $\Delta H^\circ_{f,298}$ are 19−21 kJ mol^{-1} higher than the experimental estimate (582 kJ mol^{-1}).[8,11c] However, 298 K corrections due to the enthalpy contents of $\mathbf{5a}^{\bullet+}$ or $\mathbf{6a}^{\bullet+}$ (Table 4) and ethylene or propene bring the experimental value to 607 kJ mol^{-1} in good agreement with the calculated one.

The experimental datum has been corrected previously to 601 kJ mol^{-1} by empirical correlations with the $\Delta H_{f,298}$ of the lower enol ions.[8b]

Enol Ionization Energies. In contrast to the enthalpies of formation, which are derived data, ionization energies are obtained by direct measurements, and comparison of the calculated and experimental data is therefore of interest and relevance. Ab initio calculations typically underestimate ionization energies due to a greater correlation energy in the neutral molecule as compared to that in the cation radical. The G2(MP2) scheme treats this deficiency by including an empirical "isogyric" correction of 0.0048 hartree per valence shell electron.[20b] The latter correction appears to be too large for the present calculations as shown by comparing the calculated and experimental data for several molecules whose accurate IE are known (Table 8). Moreover, the QCISD(T) ionization energies tend to converge to the experimental values as the size of the molecule increases, e.g., from ethylene to butene (Table 8). This effect may be due to two unrelated factors. First, the size of the basis set increases with the number of atoms in the molecule and the ion, thus providing more flexible wave functions to describe the neutral and ion systems. Second, the experimental measurements of adiabatic ionization energies are more difficult for larger molecules, since the first bands in the photoelectron spectra become broader and the determination of the onset is less accurate. Instead of using a constant isogyric term, we implement the ΔIE values of the corresponding olefins, e.g. ethylene for **1**, propene for **2**, **3**, and **4**, and butene for **5** and **6**, to correct the calculated adiabatic ionization energies (Table 9).

Table 8. Ionization Energies[a]

species	IE_a(QCISDT)[b]	IE_a(exp)[c]	IE_a(G2)	ΔIE[d]
$CH_2{=}CH_2$	10.453	10.514	10.584	0.06
$CH_3CH{=}CH_2$	9.71	9.73	9.84	0.02
(*Z*)-2-butene	9.11	9.11	9.24	0.00
CH_3CHO	10.18	10.23	10.31	0.05
CH_3COCH_3	9.656	9.705	9.786	0.05
CH_3CH_2CHO	9.99	9.96	10.12	−0.03

[a] In units of eV. [b] From QCISD(T)/6-311+G(3df,2p) calculations (Table 1−4, eq 1) with HF/6-31+G(d,p) zero-point corrections. [c] From ref 44. [d] $\Delta IE_a = IE_a(\mathrm{exp}) - Ie_a(\mathrm{QCISDT})$.

Table 9. Ionization Energies of Enols[a]

species	IE_a(QCISDT)[b]	IE(exp)	IE_{corr}[b]	IE_{therm}[c]	IE_v
1s	9.21		9.27	9.28	9.51
1a	9.08	9.17[d]	9.14	9.16	9.40
2s	8.75		8.77	8.79	9.10
2a	8.64	8.67[e]	8.66	8.69	9.00
3s	8.66		8.68	8.69	8.96
3a	8.55	8.64[e]	8.57	8.57	8.86
4s	8.69		8.71	8.71	8.99
4a	8.57	8.70[e]	8.59	8.59	8.88
5s	8.25		8.25	8.26	8.60
5a	8.13	8.42[e]	8.13	8.15	8.59
6s	8.30		8.30	8.32	8.63
6a	8.19	8.44[e]	8.19	8.21	8.58

[a] In units of eV. [b] Corrected by the ΔIE for the corresponding alkene. [c] From $\Delta H^\circ_{f,298}$(ion rotamer) − $\Delta H^\circ_{f,298}$(neutral rotamer). [d] From the photoelectron spectrum of **1**, ref 17b. [e] From electron impact threshold measurements, refs 8b and 10.

The adiabatic and vertical ionization energies of **1s** and **1a** differ as expected from the different relative stabilities of the syn and anti rotamers for the neutral enols and the cation radicals (Table 5). The corrected $IE_a(\mathbf{1a})$ compares very well with the experimental data from photoelectron spectra (9.17 and 9.18 eV)[17] and an electron impact measurement (9.14 eV).[9] The value calculated from the neutral and ion enthalpies of formation, $IE_{therm} = \Delta H^\circ_{f,298}$(ion rotamer) − $\Delta H^\circ_{f,298}$(neutral rotamer) (Table 9), is in an excellent agreement with the experimental data. It should be noted, however, that the IE_{therm} datum includes, through the corresponding enthalpies of formation, the experimental ionization energies of the auxiliary molecules used to evaluate the isodesmic reactions. Nevertheless, the agreement between the calculated and experimental data indicates that the

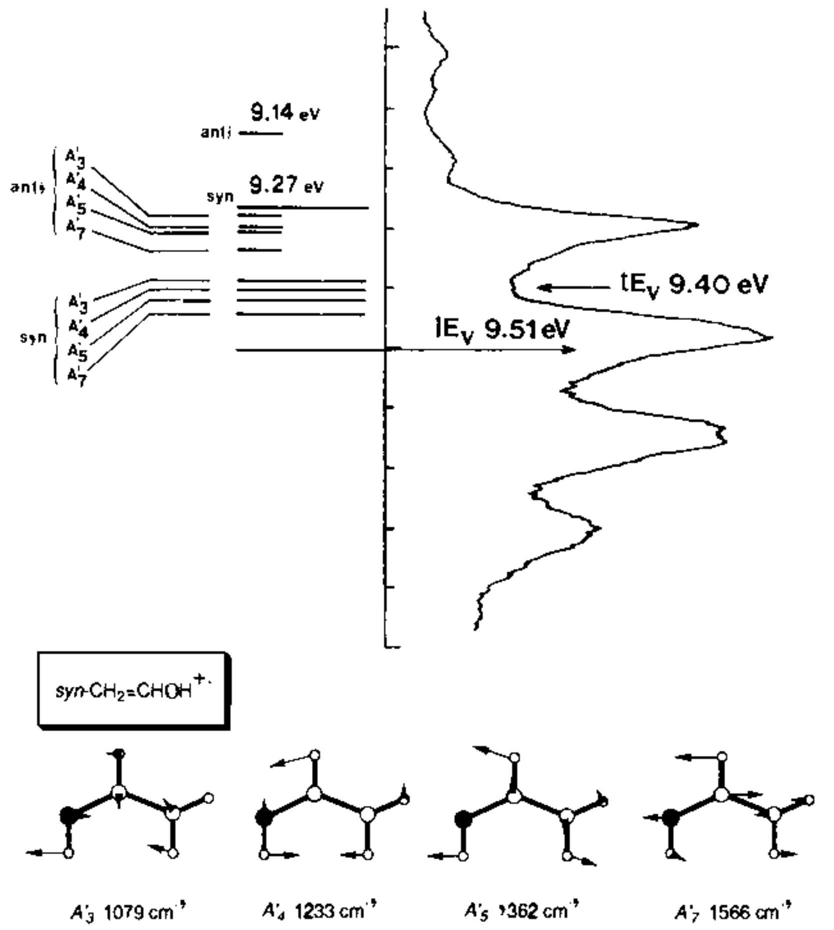

Figure 8. Fine structure assignment of the first band in the photoelectron spectrum of **1** (ref 17b).

neutral and ion potential energy surfaces for **1** are connected accurately at the present level of theory.

Experimental adiabatic and vertical IE of **1s** have been assigned in the photoelectron spectrum,[17b] which showed vibrational progressions estimated at 1330 and 1400 cm^{-1}. The vibrational progression upon ionization of **1s** and **1a** originates from the A'$_3$, A'$_4$, A'$_5$, and A'$_7$ modes that are excited in the ions due to different bond lengths and angles in the molecules and the cation radicals as shown for **1s**$^{\cdot+}$ (Figure 8). Using the corrected harmonic frequencies of the excited modes, one can reinterpret the photoelectron spectrum of **1** as follows. The weak band with an onset at ~9.12 eV corresponds to ionization of the less populated isomer **1a** of IE$_a$ = 9.14 eV. The vibrational progression of this band at 9.28–9.33 eV and the band of IE$_v$(**1a**) at 9.40 overlap with the band for the IE$_a$(**1s**) at 9.27 eV and its vibrational progression at 9.40–9.46. The latter further overlaps with the band of IE$_v$(**1s**) at 9.51. It should be noted that the C–OH torsional mode (A''$_1$) is substantially excited in the neutral enols. From the corresponding Boltzmann factors[52] one can estimate 15 and 43% of $v \geq 1$ in **1s** and **1a**, respectively, at 298 K. Hence the photoelectron bands are likely to be broadened by ~0.05 eV due to unresolved A''$_1$ $0 \rightarrow 0'$, $1 \rightarrow 0'$, and $1 \rightarrow 1'$ transitions.

The calculated IE$_{\text{vert}}$ and IE$_{\text{therm}}$ for **2a** show good agreement with the experimental IE from threshold electron impact measurements.[11b] Both rotamers of **2** are significantly populated at the temperature of the experiment, and so the true threshold value should correspond to the smaller IE(**2a**), provided that ionization of **2a** is not overly disfavored by small Franck–Condon factors. Fair agreement is obtained for **3** and **4**, where the calculated IE's of the rotamers bracket the experimental values.[11c] By contrast, the calculated IE$_a$ and IE$_{\text{therm}}$ for **5** and **6** are 0.25–0.29 eV lower than the experimental threshold ionization energies.[8b] The reason for this discord is unclear, although it is possible that the experimental data could be affected by unfavorable Franck–Condon factors,[11c] which would result in upward shifts in the threshold data.

Conclusions

Ab initio calculations using isodesmic and isogyric reactions are found to provide consistent gas-phase enthalpies of formation of vinyl alcohol, 2-propenol, (*E*)- and (*Z*)-1-propenol, (*E*)- and (*Z*)-2-butenol, and their corresponding cation radicals. The two sets of data are linked with ionization energies that mostly show satisfactory agreement with experimental data.

Syn isomers are thermochemically more stable for the entire series of neutral enols and are mostly favored at thermal equilibrium. The **4s** ⇌ **4a** system is an exception, whereby the isomer populations are similar. Extrapolation of the calculated gas-phase $\Delta G°_{298}$(enol–oxo) to aqueous solution shows for the first time a reasonable agreement with previous equilibrium measurements.

Anti isomers are uniformly favored for the enol cation radicals and predicted to dominate at thermal equilibrium. The calculated enthalpies of formation show good agreement with previous experimental estimates for **1**, **1**$^{\cdot+}$, and **2**, but diverge significantly for **2**$^{\cdot+}$, **3–6**, and **3**$^{\cdot+}$–**6**$^{\cdot+}$. The differences are attributed to underestimated $\Delta H°_{f,298}$ values from the measurements and can be largely removed by including 298 K enthalpy corrections in the experimental appearance energies.

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Supporting Information Available: Tables of optimized geometries in a Z-matrix format and harmonic frequencies (11 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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