Notes

Thermochemistry of Unstable Enols: The O-(C_d)(H) Group Equivalent

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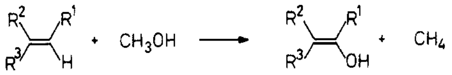
Benson's additivity rules[1,2] represent a reliable and convenient means for the estimation of thermochemical properties of organic compounds. The system is based on a large set of experimental thermochemical data[3] (mostly heats of formation, ΔH_f^0) for compounds of various structural types and enables interpolation and extrapolation for those unknown compounds that are composed of structural units included in the set.[1] In this way, reaction enthalpies can be predicted with chemical accuracy (within ± 5 kJ·mol^{-1}) provided both the reactants and the products can be treated by the additivity rules.

A logical step to further expand the system would be to estimate thermochemical properties of kinetically unstable compounds that appear as intermediates of organic reactions and that have impact on reaction kinetics. Simple enols[4] have been considered or proven to be reactive intermediates in a number of organic reactions, e.g., electrophilic substitutions in aldehydes and ketones,[5] oxy-Cope,[6] Conia[7] and Carroll rearrangements,[8] retro-Diels–Alder reaction,[9] enol ether hydrolysis,[10] etc. Since, however, simple enols have very short lifetimes in the condensed phase,[11] their heats of formation cannot be determined by classical methods, i.e., from heats of combustion or hydrogenation. An alternative approach to thermochemistry of unstable enols relies upon ionization of the neutral enol in the gas phase and dissociative ionization of a suitable stable precursor to form the ionized enol. The threshold (ideally adiabatic) ionization energy of the enol and the heat of formation of the corresponding cation radical then give the heat of formation of the neutral species (eq 1).[12]

$$\Delta H_f^0(\text{enol}) = \Delta H_f^0([\text{enol}]^+) - \text{IE}(\text{enol}) \qquad (1)$$

Scheme I



R^1 = H, CH_3, $CH{=}CH_2$, $C{\equiv}CH$

R^2, R^3 = H, CH_3, $CH{=}CH_2$, OH

In the present paper we report experimental heats of formation, obtained from eq 1, for nine simple enols of different types, e.g., vinyl alcohol (**1**), 1-propen-2-ol (**2**), (*E*)- and (*Z*)-1-propen-1-ol (**3** and **4**), (*E*)- and (*Z*)-1-hydroxybuta-1,3-diene (**5** and **6**), 2-hydroxybuta-1,3-diene (**7**), 2-hydroxybut-1-en-3-yne (**8**), and (*Z*)-ethene-1,2-diol (**9**) (Table I). These enols have been prepared earlier[12,13] and their ionization energies were determined by photoelectron[13b] or, more frequently, electron-impact ionization techniques.[12,13a,c–g] The experimental ΔH_f^0 values are compared with those calculated by the semiempirical MNDO method.[14]

The data confirm that simple enols are as a rule less stable than the corresponding oxo forms.[4] An exception is encountered with **5** and **6**, which are calculated to be more stable than the unconjugated aldehyde, 3-butenal.[13g] Aside from vinyl alcohol, the differences in enthalpies for enols vs. aldehydes (Table I, entries **3–6**) and enols vs. ketones (Table I, entries **2**, **7**, **8**) show only minor differences within the given series, suggesting that the effect of an alkyl, alkenyl, or alkynyl substituent is similar in the enol and oxo systems. From the ΔH_f^0 values it follows that the enols **1–8** will exist in minute concentrations in equilibrium mixtures.[15] The enediol **9** is estimated to be only slightly destabilized against glycol aldehyde and should be found in a detectable concentration at an enol–oxo equilibrium, provided there are no adverse entropy effects beside those of symmetry.[16]

Semiempirical calculations of the ΔH_f^0 by MNDO are in good-to-excellent agreement with experiment. The greatest deviation is found with the enediol **9**, whose syn,anti form is calculated to be more stable than glycolaldehyde, in contradiction to experiment.[16] This dis-

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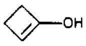
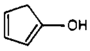
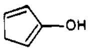
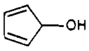
Table I. Thermochemical Data of Enols 1–9

entry	enol	ΔH_f^0(ion)[a]	IE, eV	ΔH_f^0(neutral)[a] exptl	MNDO	ΔH_f^0(enol–oxo)[b]	ΔH_r[a]
1	$CH_2{=}CHOH$	758[c]	9.18[d]	–128	–146[e]	38	54
2	$CH_2{=}C(OH)CH_3$	661[f]	8.67[g]	–176	–179[e]	42	70
3	(*E*)-$CH_3CH{=}CHOH$	665[f]	8.64[h]	–169	–187[e]	23	64
4	(*Z*)-$CH_3CH{=}CHOH$	665[f]	8.70[h]	–174	–186	18	68
5	(*E*)-$CH_2{=}CHCH{=}CHOH$	733[i]	8.51[i]	–88	–89[i]	19[j] (–8)[k]	72
6	(*Z*)-$CH_2{=}CHCH{=}CHOH$	728[i]	8.47[i]	–90	–87[i]	17[j] (–10)[k]	74
7	$CH_2{=}CHC(OH){=}CH_2$	761[l]	8.68[m]	–77	–73	35	61
8	$HC{\equiv}CC(OH){=}CH_2$	944[n]	8.92[n]	83	77	33	78
9	(*Z*)-$OHCH{=}CHOH$	516[o]	8.62[o]	–316	–355	2	62

[a] kJ·mol^{-1}; the uncertainty in the ionic heats of formation is within 5–10 kJ·mol^{-1}. Standard deviations in ionization energy measurements are 2–3 kJ·mol^{-1}. [b] Positive values mean that the enol is less stable than the corresponding oxo form. [c] Reference 21. [d] Reference 13b. [e] Reference 22. [f] Reference 23. [g] Reference 13c. [h] Reference 13d. [i] Reference 13g. [j] Referred to (*E*)-2-butenal.[1] [k] Referred to the estimated[1,2] ΔH_f^0 of 3-butenal. [l] Reference 24. [m] Reference 13e. [n] Reference 13f. [o] Reference 25.

Table II. Estimated ΔH_f^0 (kJ•mol^{-1}) for Enols 10–15

entry	enol	ΔH_f^0	ΔH_f^0 (enol–keto)
10		–26	*a*
11		–59	31[b]
12		–57	33[b]
13		–27	
14	$CH_3C(OH){=}CHCOCH_3$	(–352)	(26)[c]
15	$CH_3C(OH){=}CHCOOCH_3$	(–524)	(35)[d]

[a] The experimental ΔH_f^0 of cyclobutanone is unknown. [b] Referred to the estimated[1,2] ΔH_f^0 of 2-cyclopenten-1-one. [c] Referred to the ΔH_f^0 of pentane-2,4-dione.[2] [d] Referred to the estimated[2] ΔH_f^0 of methyl acetoacetate.

crepancy is probably due to the known failure of MNDO[14] to evaluate correctly hydrogen bonds.

In contrast to the enol–oxo isomerism, placing the hydroxyl group onto a double bond has invariantly a *stabilizing* effect, as also predicted by high-level ab initio calculations.[17] The estimated enthalpy changes in isodesmic reactions[18] (Scheme I, ΔH_r in Table I) oscillate around 67 ± 7 kJ·mol^{-1} and show that the enolic hydroxy group can be treated as an entity in the sense of Benson's rules.[1,2] Thence we calculate the corresponding term for the O–(C_d)(H) group as –202 ± 6 kJ·mol^{-1}, which is somewhat lower than reported earlier on the basis of ionization energies of **1** and **2** (–186 kJ·mol^{-1}).[12] The revised value can be utilized for predicting the heats of formation of other enols, especially those which are at present hardly accessible by standard synthetic procedures.[9,10] (Table II).

Cyclobutenol (**10**) is estimated to be substantially less stable than **7**, and it would isomerize to the latter dienol via symmetry-allowed conrotatory ring opening.[19] By contrast, MNDO calculations predict **10** to be more stable than **7** (ΔH_f^0 (**10**) = –84 kJ·mol^{-1}). This discrepancy with the additivity-based estimate is probably due to the underestimation of ring strain in **10**, a known feature of the MNDO method.[26]

Hydroxycyclopentadienes **11**–**13** would be difficult to prepare by thermolytic methods as distinct isomers, because of rapid 1,5-suprafacial hydrogen migration across the ring.[27] The estimated ΔH_f^0 values for the isomers indicate that the dienols **11** and **12** are of comparable stability, while being more stable than the hydroxy diene **13** in which the hydroxyl is located outside the diene system (Table II). This is consistent with the stabilization of the double bonds by attachment of the hydroxy group.[17] MNDO calculations yield ΔH_f^0 (**12**) = –60 kJ·mol^{-1} in good agreement with the additivity-based prediction (Table II).

The limits of applicability of Benson's rules are crossed with the stable[20] enols **14** and **15** for which the group additivity scheme predicts substantial destabilization against pentane-2,4-dione and methyl acetoacetate, respectively (Table II). This disagreement points to a stabilizing long-range interaction in the enols, e.g., a strong intramolecular hydrogen bond, which is not taken into account by the additivity principle.[1] Further experiments are needed to clarify this point.

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Synthesis of *proximal*-Benzoguanine and a Simplified Synthesis of *proximal*-Benzohypoxanthine

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Benzo-separated purines and purine nucleosides have been used to analyze the binding domains of purine-utilizing or metabolizing enzymes.[1] These studies have produced many benzo-separated systems.[1–6] However,

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