Table III. Total Energies (Hartrees), Bond Energy, and Geometries for SF_2, SF_2^+, and $(SF_2)_2^+$

	SF_2	SF_2^+	$(SF_2)_2^+$	ΔH^a
3-21G(*)	−593.418 870	−593.074 529	−1186.508 443	−9.44
6-31G	−596.200 809	−595.791 094	−1191.997 781	−3.69
6-31G*	−596.312 151	−595.971 582	−1192.296 798	−8.20
PMP2/6-31G	−596.502 353	−596.100 232	−1192.618 321	−9.88
[PMP2/ 6-31G*]				−14.39
geometry (3-21G(*))	S–F 1.592 F–S–F 98.3	S–F 1.516 F–S–F 100.5	S–F 1.551 S–S 2.866 F–S–F 99.4 tilt[b] 88.1	

[a] In kcal/mol, for $SF_2 + SF_2^+ \rightarrow (SF_2)_2^+$. [b] Angle between the S–S bond and the line bisecting the F–S–F angle. The lines bisecting the F–S–F angles form a dihedral angle of 180°.

calculations indicated that the $(H_2S)_2^+$ dimer is more appropriately described as H_3S^+ bound by electrostatic forces to an SH radical. Therefore, the structures of the neutral van der Waals molecule, $(H_2S)_2$, and of the dimer ion, $(H_2S)_2^+$, might not pertain to a 2c 3e bond. Our calculations and those of Clark on the $H_2S + H_2S^+$ system should be viewed as didactic exercises designed to illuminate the nature of the 2c 3e S–S bond in a computationally simple system rather than calculations aimed at explaining experimental results, which, as Fernandez et al. point out, may not be measuring the strength of a $[H_2S\text{- - -}SH_2]^+$ sulfur–sulfur bond. (There is evidence, nonetheless, for the existence of $[H_2S\text{- - -}SH_2]^+$ in aqueous solution.)[26]

On the other hand, it is difficult to envision the $(CH_3)_2S + (CH_3)_2S^+$ system involving anything other than a 2c 3e S–S bond. Therefore, our calculations on this system may be compared directly and unambiguously to our experimental data. At the [PMP2/6-31G*]//3-21G(*) level (brackets indicate that the additivity approximation[27] was used), a $\Delta H°$ of −27.4 kcal/mol is calculated (see Table II). This value may be improved in an approximate way by applying the zero-point correction from the H_2S system, as well as the correction found in the H_2S system on going from [PMP2] to the full PMP4 level. The $\Delta H°$ obtained in this way is −25.5 kcal/mol, which is in excellent agreement with the range of values derived from the experimental measurements.

In order to explore substituent effects on 2c 3e bond energy, the $SF_2 + SF_2^+$ system was calculated (see Table III). At the [PMP2/6-31G*]//3-21G(*) level a $\Delta H°$ of −14.4 kcal/mol was found. When we applied the same "corrections" here as were applied in the $(CH_3)_2S + (CH_3)_2S^+$ case, the $\Delta H°$ obtained is −12.2 kcal/mol, which is about half the bond energy calculated for the non-fluorine-containing cases.

Note Added in Proof: Gill and Radom have recently reported the same theoretical binding energy for $(H_2S)_2^+$, namely 26.5 kcal/mol.[28]

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(26) Chaudhri, S. A.; Asmus, K.-D. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 672–673.

(27) (a) McKee, M. L.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1981**, *103*, 4673. (b) Nobes, R. H.; Bouma, W. J.; Radom, L. *Chem. Phys. Lett.* **1982**, *89*, 497. (c) McKee, M. L.; Lipscomb, W. N. *Inorg. Chem.* **1985**, *24*, 762.

(28) Gill, P. M. W.; Radom, L. *J. Am. Chem. Soc.* **1988**, *110*, 4931–4941.

Unstable Enols in the Gas Phase. Preparation, Ionization Energies, and Heats of Formation of (*E*)- and (*Z*)-2-Buten-2-ol, 2-Methyl-1-propen-1-ol, and 3-Methyl-2-buten-2-ol

František Tureček,*,† Libor Brabec,‡ and Jorma Korvola*,§

Contribution from Baker Laboratory, Department of Chemistry, Cornell University, Ithaca, New York 14853-1301, The J. Heyrovsky Institute of Physical Chemistry and Electrochemistry, Czechoslovak Academy of Sciences, Prague, Czechoslovakia, and the Department of Chemistry, University of Jyväskylä, Kyllikinkatu 1-3, SF-40100 Jyväskylä, Finland. *Received April 20, 1988*

Abstract: (*E*)-2-Buten-2-ol (**1**), (*Z*)-2-buten-2-ol (**2**), 2-methyl-1-propen-1-ol (**3**), and 3-methyl-2-buten-2-ol (**4**) were prepared as transient species by flash-vacuum pyrolysis of the corresponding methylated bicyclo[2.2.1]hept-5-en-2-ols and characterized by mass spectrometry. Threshold ionization energies (IE) were determined as IE(**1**) = 8.42 ± 0.04, IE(**2**) = 8.44 ± 0.03, IE(3) = 8.44 ± 0.03, and IE(**4**) = 8.15 ± 0.04 eV. Cation radical $[4]^{\bullet+}$ was generated from 3,3-dimethyl-2-hexanone, and its appearance energy and heat of formation were determined as AE = 9.33 ± 0.09 eV and $\Delta H_f° = 545 \pm 10$ kJ·mol⁻¹. The heats of formation of the neutral enols **1–4** were determined as −212, −214, −207, and −241 kJ·mol⁻¹, respectively. The experimental heats of formation are compared with those predicted from Benson's additivity rules or calculated by the semiempirical MNDO method. Substituent effects on the heats of formation, proton affinities, and relative thermochemical and kinetic stabilities of simple enols are discussed.

Simple enols[1] appear as transient intermediates in a variety of fundamental organic reactions, namely aldol condensation,[2] electrophilic substitution in carbonyl compounds,[3] oxy-Cope,[4] Conia,[5] and Caroll rearrangements,[6] and others.[7] In view of the key role enols play in the kinetics of several organic reactions, there is demand for thermodynamic data that would allow the quan-

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[†] Cornell University.

[‡] Czechoslovak Academy of Sciences.

[§] University of Jyväskylä.

(1) Hart, H. *Chem. Rev.* **1979**, *79*, 515.

(2) House, H. O. *Modern Synthetic Reactions*, 2nd ed.; Benjamin: Menlo Park, 1972; Chapter 10, pp 629–733.

(3) (a) Toullec, J.; El-Alaoui, M. *J. Org. Chem.* **1986**, *51*, 4054. (b) Toullec, J. *Adv. Phys. Org. Chem.* **1982**, *18*, 1.

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titative treatment of these reactions.[8a,9] Due to their kinetic instability with respect to isomerization into the more stable oxo forms (aldehydes or ketones), simple enols exist only in minute concentrations under equilibrium conditions in both the gas phase[8b] and solution.[3] Investigation of such equilibria is experimentally difficult and has sometimes yielded controversial results.[8a,10]

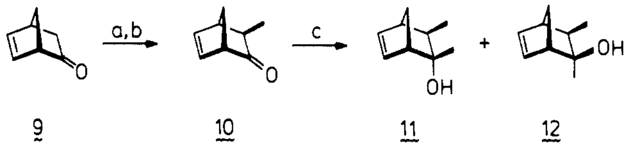
An alternative approach to the thermochemistry of unstable enols rests on gas-phase reactions involving ionization of the enol to the corresponding cation radical (eq 1), combined with dissociative ionization of a stable precursor producing the same enolic ion (eq 2). The reaction enthalpies, i.e. the threshold (ideally adiabatic) ionization energy (IE) in eq 1, and the appearance energy (AE) in eq 2 make it possible for one to calculate[11] the heat of formation of the unstable enol involved.[12] This straightforward approach has been used to determine heats of formation of a number of simple enols of various structural types[12,13] and has eventually afforded the enthalpy term for the enolic hydroxy group, $[\mathrm{O{-}(C_d)(H)}] = -202 \pm 6$ kJ·mol^{-1}.[13j] The latter term, when incorporated into Benson's additivity rules,[14] has proven to be useful for predicting gas-phase heats of formation of other enol systems,[13j] e.g. 1-phenylethanol ($\Delta H_f°$: found, −46 kJ·mol^{-1};[13h] estimated, −47 kJ·mol^{-1}) or 1-buten-2-ol ($\Delta H_f°$: found, −196 kJ·mol^{-1};[13i] estimated, −195 kJ·mol^{-1}).

$$\text{enol} \rightarrow [\text{enol}]^{\bullet+} \qquad (1)$$

$$\text{precursor} \rightarrow [\text{enol}]^{\bullet+} + \text{neutral molecule} \qquad (2)$$

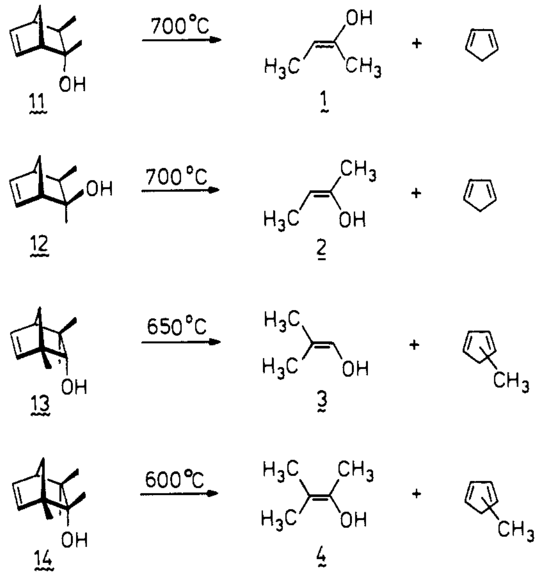
Applications of the additivity rules to the thermochemistry of enols fail if the latter involve strong hydrogen bonds[13j,15] or steric interactions of unknown magnitude. For instance, triaryl-substituted enols are estimated by the additivity scheme to be less stable than the corresponding ketones, while both qualitative[16] and quantitative studies[17] have proven to the contrary, having shown that these enols have often been the more stable. Steric effects have been noted to contribute significantly to the reversed order of stabilities in aryl-substituted ethenols.[17,18] By contrast, the normal order of stability has been observed for the system 1-phenylethenol–acetophenone in both solution[3a,19] and the gas phase.[13h]

Scheme I[a]



[a] Key: (a) LDA/THF, −78 °C; (b) MeI, 3–5 equiv, −40 to 0 °C, 2 h; (c) MeMgI, Et$_2$O, 0 °C.

Scheme II



The substituent effects on the enol–oxo relative stabilities in aryl-substituted enols are the resultant of steric and conjugative interactions that are not easily separated.[17,18] The steric effects can be studied in a more straightforward way with aliphatic systems. Various trialkyl-substituted enols have been generated in solution and found to rapidly isomerize to ketones.[20] Quantitative data are available for 2-methyl-1-propen-1-ol (**3**), which has been found to be destabilized against isobutyraldehyde by $\Delta\Delta G° = 22$ kJ·mol^{-1} in dilute aqueous solution.[21]

The objective of the present paper is to determine gas-phase heats of formation for (*E*)-2-buten-2-ol (**1**), (*Z*)-2-buten-2-ol (**2**), 2-methyl-1-propen-1-ol (**3**), and 3-methyl-2-buten-2-ol (**4**). Together with ethenol (**5**), (*E*)- and (*Z*)-1-propen-1-ol (**6** and **7**), and 1-propen-2-ol (**8**) whose heats of formation have been known,[12,13a–d,j] compounds **1–4** will make a complete series of methyl-substituted enols for the examination of alkyl substituent effects on the enol–oxo relative stabilities.

Results

Preparation and Characterization. Simple enols can be generated in high yield by the retro-Diels–Alder decomposition of bicyclo[2.2.1]hept-5-ene or 9,10-ethano-9,10-dihydroanthrancene precursors,[7,13a,c–b,j,22] carried out under conditions of flash-vacuum pyrolysis. The former precursors appear to be much more suitable for the purposes of mass spectral analysis as the ionization cross section of the by-produced cyclopentadiene is smaller than that of anthracene. To this end we prepared 2-*exo*-3-*exo*-dimethylbicyclo[2.2.1]hept-5-en-2-ol (**11**) and its 2-*endo*-methyl isomer (**12**), which served as precursors for **1** and **2**, respectively. The two-step preparation of **11** and **12** required subsequent introduction of two methyl groups in bicyclo[2.2.1]hept-5-en-2-one (**9**, Scheme

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(4) Berson, J. A.; Jones, M., Jr. *J. Am. Chem. Soc.* **1964**, *86*, 5019.

(5) Conia, J. M.; LePerchec, P. *Synthesis* **1975**, 1.

(6) Cookson, R. C.; Parsons, P. J. *J. Chem. Soc., Chem. Commun.* **1976**, 990.

(7) Ripoll, J.-L. *Nouv. J. Chim.* **1979**, *3*, 195 and references therein.

(8) (a) Guthrie, J. P.; Cullimore, P. A. *Can. J. Chem.* **1979**, *57*, 240. (b) Slanina, Z. *Chem. Phys. Lett.* **1984**, *105*, 531.

(9) Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley: New York, 1976.

(10) Dubois, J. E.; El-Alaoui, M.; Toullec, J. *J. Am. Chem. Soc.* **1981**, *103*, 5393.

(11) Traeger, J. C.; McLoughlin, R. G.; Nicholson, A. J. C. *J. Am. Chem. Soc.* **1982**, *104*, 5318.

(12) Holmes, J. L.; Lossing, F. P. *J. Am. Chem. Soc.* **1982**, *104*, 2648.

(13) (a) Tureček, F.; Hanuš, V. *Org. Mass Spectrom.* **1984**, *19*, 423. (b) Albrecht, B.; Allan, M.; Haselbach, E.; Neuhaus, L.; Carrupt, P.-A. *Helv. Chim. Acta* **1984**, *67*, 216. (c) Tureček, F.; Hanuš, V. *Org. Mass Spectrom.* **1984**, *19*, 631. (d) Tureček, F. *J. Chem. Soc., Chem. Commun.* **1984**, 1374. (e) Tureček, F. *Tetrahedron Lett.* **1984**, *25*, 5133. (f) Tureček, F.; Havlas, Z.; Maquin, F.; Gäumann, T. *Helv. Chim. Acta* **1986**, *69*, 683. (g) Tureček, F.; Havlas, Z.; Maquin, F.; Hill, N.; Gäumann, T. *J. Org. Chem.* **1986**, *51*, 4061. (h) Tureček, F. *Tetrahedron Lett.* **1986**, *27*, 4219. (i) Iraqi, M.; Pri-Bar, I.; Lifshitz, C. *Org. Mass Spectrom.* **1986**, *21*, 661. (j) Tureček, F.; Havlas, Z. *J. Org. Chem.* **1986**, *51*, 4066.

(14) Benson, S. W.; Cruickshank, F. R.; Golden, D. M.; Haugen, G. R.; O'Neal, H. E.; Rodgers, A. S.; Shaw, R.; Walsh, R. *Chem. Rev.* **1969**, *69*, 279.

(15) Bouchoux, G.; Hoppilliard, Y.; Houriet, R. *Nouv. J. Chim.* **1987**, *11*, 226.

(16) (a) Fuson, R. C.; Corse, J.; McKeever, C. H. *J. Am. Chem. Soc.* **1940**, *62*, 3250. (b) Fuson, R. C.; Byers, D. J.; Rabjohn, N. *J. Am. Chem. Soc.* **1941**, *63*, 2369. (c) Fuson, R. C.; Chadwick, D. H.; Ward, M. L. *J. Am. Chem. Soc.* **1946**, *68*, 389.

(17) (a) Biali, S. E.; Rappoport, Z. *J. Am. Chem. Soc.* **1985**, *107*, 1007. (b) Nugiel, D. A.; Rappoport, Z. *J. Am. Chem. Soc.* **1985**, *107*, 3669. (c) Nadler, E. B.; Rappoport, Z. *J. Am. Chem. Soc.* **1987**, *109*, 2112.

(18) Miller, A. R. *J. Org. Chem.* **1976**, *41*, 3599.

(19) Toullec, J. *Tetrahedron Lett.* **1984**, *25*, 4401.

(20) (a) Hoffmann, H. M. R.; Schmidt, E. A. *J. Am. Chem. Soc.* **1972**, *94*, 1373. (b) Schmidt, E. A.; Hoffmann, H. M. R. *J. Am. Chem. Soc.* **1972**, *94*, 7832. (c) Hoffmann, H. M. R.; Clemens, K. E.; Schmidt, E. A.; Smithers, R. H. *J. Am. Chem. Soc.* **1972**, *94*, 3201.

(21) (a) Chiang, Y.; Kresge, A. J.; Walsh, P. A. *J. Am. Chem. Soc.* **1982**, *104*, 6122. (b) Chiang, Y.; Kresge, A. J.; Walsh, P. A. *J. Am. Chem. Soc.* **1986**, *108*, 6314.

(22) Lasne, M.-C.; Ripoll, J.-L. *Synthesis* **1985**, 121.

Table I. 75-eV Mass Spectra of **1**–**4**

	relative abundance, %				relative abundance, %		
m/z	**1, 2**	**3**	**4**	*m/z*	**1, 2**	**3**	**4**
87			6	45	7	9	6
86			96	44	4	3	3
85			5	43	100	49	100
73	2	6		42	6	12	6
72	43	89	4	41	11	72	43
71	14	14	72	40	5	16	10
70	1		3	39	16	39	11
69			5	38	4	25	9
68			2	37	3	14	4
59			2	31	6	18	4
58		5	6	29	14	47	9
57	24	100	9	28	3	16	–
56	2		1	27	26	82	26
55	5	9	6	26	9	13	5
54	2	7		15	13	9	10
53		18	9	14	3		2

I).[23] In contrast to a recent report,[24] we have encountered no unsurmountable difficulties in the methylation of the lithium enolate of **9**.[25] Ketone **10** was reproducibly obtained in 50% yield and 95% purity (by GC) after simple fractional distillation. The minor contaminants were **9** (4%) and a dimethyl derivative (1%). The tri- and tetramethylated bicyclo[2.2.1]hept-5-en-2-ols **13** and **14** have been prepared earlier.[26]

Flash-vacuum pyrolysis of **11**–**14** proceeded smoothly at relatively low temperatures and low pressure, typically 10^{-6} Torr (Scheme II). Conversions were followed by mass spectrometry at 75- or 12-eV ionizing electron energy. As the precursors **11**–**14** do not afford abundant molecular ions, the conversions were monitored by the relative intensities of ions due to **1**–**4** and cyclopentadiene or methylcyclopentadiene in dependence on temperature.

The 12-eV mass spectra of **11** and **12**, taken at 100 °C, are dominated by ions $[\mathbf{1}]^{\bullet+}$ and $[\mathbf{2}]^{\bullet+}$, respectively. At 620 °C the relative intensity of $[C_5H_6]^{\bullet+}$ starts increasing to reach a maximum at 700 °C. In the 75-eV mass spectrum recorded at this oven temperature the $[C_5H_5]^+/[C_5H_6]^{\bullet+}$ abundance ratio ranged between 0.52 and 0.55 corresponding to free cyclopentadiene. The 75-eV mass spectra of **1** and **2**, obtained after having subtracted from the spectra of the pyrolysates a standard spectrum of cyclopentadiene, are indistinguishable, and both can be represented by the spectrum given in Table I. The latter differs from the spectrum of 2-butanone[27] by the presence of $[C_4H_7O]^+$ at *m/z* 71, $[C_3H_3O]^+$ at *m/z* 55, and $[CH_3O]^+$ at *m/z* 31. Also, the relative abundances of the molecular ions $[\mathbf{1}]^{\bullet+}$ and $[\mathbf{2}]^{\bullet+}$ are higher than that of 2-butanone.[27] The presence of abundant fragments at *m/z* 71, 55, and 31 is typical of the enolic structures $[\mathbf{1}]^{\bullet+}$ and $[\mathbf{2}]^{\bullet+}$ according to their collisionally activated decomposition (CAD) spectra.[28] The mass spectra of both 2-buten-2-ols are significantly different from the published mass spectrum of isomeric 1-buten-2-ol.[13i]

Nevertheless, ionization energy measurements (vide infra) and the temperature dependence of the mass spectra indicated that both **1** and **2** contained small fractions of the keto form. When the pyrolyzer temperature was increased up to 850 °C, the relative intensity of $[C_4H_8O]^{\bullet+}$ decreased, while that of $[C_2H_3O]^+$ increased, consistent with the more efficient coformation of 2-butanone. Under optimized conditions at 700 °C the content of the latter in the pyrolysates can be estimated as 10–20%. Hence, the reported mass spectrum of **1** and **2** (Table I) contains contributions from 2-butanone at *m/z* 29, 43, 57, and 72.

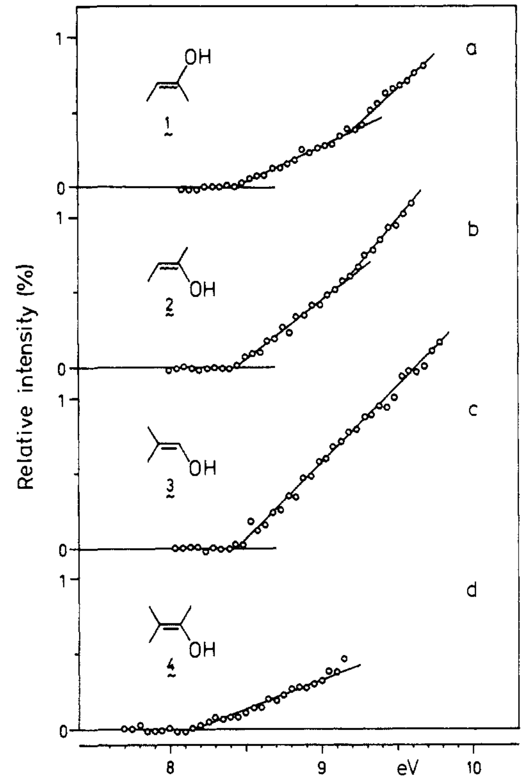

Figure 1. Deconvoluted ionization-efficiency curves for (a) **1**, (b) **2**, (c) **3**, and (d) **4**.

Pyrolysis of **13** became observable at 570 °C as judged by the changes in the relative abundances of $[C_4H_8O]^{\bullet+}$ and $[C_6H_7]^+$ in the 75-eV mass spectrum of **13**. At 650 °C the pyrolysis was nearly complete and the abundance ratio $[C_6H_7]^+/[C_6H_8]^{\bullet+}$ reached the value given for methylcyclopentadiene.[27] Subtraction of the standard spectrum of the latter[27] from the spectrum of the pyrolysate afforded the spectrum of **3** in Table I. Unlike the mass spectrum of isobutyraldehyde,[27] enol **3** shows abundant $[C_4H_8O]^{\bullet+}$, $[C_3H_5O]^+$, $[C_4H_5]^+$, and $[CH_3O]^+$, whereas $[C_4H_7O]^+$, $[C_3H_7]^+$, and $[CHO]^+$ are less prominent. On the basis of the unique $[M - CH_3]^+/[M]^{\bullet+}$ abundance ratio in the spectrum of **3**, we assume that the enol may contain only traces of isobutyraldehyde. The facile loss of methyl from **3** upon electron impact is in line with the CAD of stable $[\mathbf{3}]^{\bullet+}$, which also gives $[C_3H_5O]^+$ as the most abundant daughter ion.[28]

Pyrolysis of **14** started at 530 °C as evidenced by the increasing relative intensities of $[C_6H_7]^+$ and $[C_6H_8]^{\bullet+}$, and it was complete at 600 °C. The 75-eV mass spectrum of **4** (Table I) differs significantly from the standard spectrum of the keto form, 3-methyl-2-butanone.[27] While the spectrum of the latter is dominated by $[C_3H_7]^+$ and $[C_2H_3O]^+$ at *m/z* 43, the former shows abundant $[C_5H_{10}O]^{\bullet+}$ at *m/z* 86 and $[C_4H_7O]^+$ at *m/z* 71. The loss of methyl producing the latter fragment ion also dominates unimolecular and collision-induced decompositions of enolic ions $[\mathbf{4}]^{\bullet+}$.[29]

The significant differences between the spectra of enols **1**–**4** on the one hand and those of their corresponding oxo forms on the other are at variance with an earlier observation of Ripoll,[7] who found no differences. We note that the success or failure in detecting simple enols by mass spectrometry crucially depends on the experimental arrangement and conditions, namely the distance of the hot zone from the ionization chamber and the temperature and surface properties of the latter. In our experience a close similarity between the spectrum of the pyrolytic product and that of the oxo form has always indicated substantial tau-

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(23) Bartlett, P. D.; Tate, B. E. *J. Am. Chem. Soc.* **1956**, *78*, 2473.

(24) Horner, J. H.; Vera, M.; Grutzner, J. B. *J. Org. Chem.* **1986**, *51*, 4212.

(25) Tureček, F.; Hanuš, V.; Gäumann, T. *Int. J. Mass Spectrom. Ion Proc.* **1986**, *69*, 217.

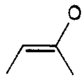
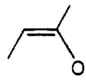
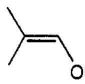
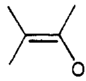
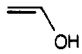
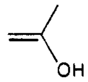
(26) Korvola, J. Dissertation, University of Jyväskylä, 1972; ISBN 951-677-027-4.

(27) Stenhagen, E.; Abrahamsson, S.; McLafferty, F. W. *Registry of Mass Spectral Data*; Wiley: New York, 1974; Vol. 1.

(28) McAdoo, D. J.; Hudson, C. E. *Org. Mass Spectrom.* **1983**, *18*, 466.

(29) McAdoo, D. J.; Hudson, C. E.; McLafferty, F. W.; Parks, T. E. *Org. Mass Spectrom.* **1984**, *19*, 353.

Table II. Thermochemical Data for Neutral Enols **1–8** and Cation Radicals $[\mathbf{1}]^{\bullet+}$–$[\mathbf{8}]^{\bullet+}$

				$\Delta H_f°$(neutral)^a		$\Delta H_r{}^a$		$\Delta H_f°$(enol–oxo)^a	
entry	enol	IE, eV	$\Delta H_f°$(ion)^a	exptl	est	exptl	est	exptl	est
			(582)^b	(−230)		(−95)		(11)	
1		8.42	601	−212	−203	−77	−68	29	37
			(582)^b	(−232)		(−93)		(9)	
2		8.44	601	−214	−207	−75	−68	27	34
3		8.44	607^b	−207	−207	−63	−63	9	9
4		8.15	545	−241	−238	−72	−69	21	24
5		9.18^c	757^b	−128		−53		38	
6		8.64^d	665^b	−169	−172	−62	−65	23	20
7		8.70^d	665^b	−174	−172	−67	−65	18	20
8		8.67^e		−176		−69		41	
		8.61^f	661^b	−170	−175	−63	−68	47	42

^{a}Kilojoules per mole. ^{b}Reference 36. ^{c}Reference 13b. ^{d}Reference 13d. ^{e}Reference 13c. ^{f}Reference 13i.

tomerization in the inlet system or the ion source.[13f,30]

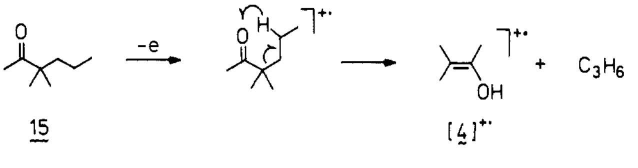
Energy Measurements. Threshold ionization energies of **1–4** were determined by electron impact ionization using the inverse convolution procedure.[31] The deconvoluted ionization-efficiency curves for **1** and **2** (Figure 1a,b) show onsets at 8.42 ± 0.04 and 8.44 ± 0.03 eV, respectively, followed by linear portions of different slopes. There are visible breaks on both curves at ca. 9.3–9.5 eV which correspond by energy to ionization of 2-butanone (IE_{vert} = 9.49–9.54 eV).[32] Evidently, the breaks cannot be due to population of the first excited state ($\tilde{A}$) in ions $[\mathbf{1}]^{\bullet+}$ or $[\mathbf{2}]^{\bullet+}$ as the energy gap between it and the ground state ($\tilde{X}$) is found to be much larger than 1 eV in ionized enols and enol ethers, e.g. 3.9 eV for ethenol[13b] and 3.0 eV for $CH_3CH{=}C(OCH_3)CH_3$.[33]

The ionization-efficiency curve of **3** (Figure 1c) shows an onset at 8.44 ± 0.03 eV, with a linear slope extending up to 10 eV. There is no detectable break below or at 9.7–9.8 eV that would indicate ionization of isobutyraldehyde (IE_{vert} = 9.71[34] or 9.82 eV[35]). This suggests that the latter oxo form was not present in the enol in any appreciable concentration (vide supra). Thus, in line with earlier findings,[7,13] the aldehyde enol is less prone to tautomerization than ketone enols.

The ionization-efficiency curve of **4** (Figure 1d) shows a well-developed linear portion near the threshold whose energy was measured as 8.15 ± 0.04 eV. Due to a small amount of **14** available for these measurements, the curve of **4** has not been investigated up to higher electron energies.

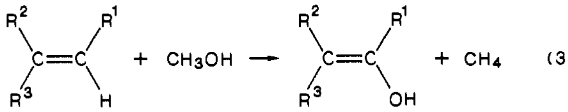
In order to calculate the heats of formation of the neutral enols **1–4** from eq 2 it is necessary to know the enthalpy data for the corresponding cation radicals. The $\Delta H_f°$ values for $[\mathbf{1}]^{\bullet+}$ (or $[\mathbf{2}]^{\bullet+}$, geometry unspecified) and $[\mathbf{3}]^{\bullet+}$ have been reported,[36] while that of $[\mathbf{4}]^{\bullet+}$ has only been estimated by extrapolation as 523 kJ·mol^{-1}.[29] In this work we generated ion $[\mathbf{4}]^{\bullet+}$ by the McLafferty rearrangement of ionized 3,3-dimethyl-2-hexanone (**15**, Scheme III). The appearance energy for $[\mathbf{4}]^{\bullet+}$ (AE = 9.33 ± 0.09 eV) combined with $\Delta H_f°$(**15**) (−335 kJ·mol^{-1} by additivity[14]) and $\Delta H_f°$($CH_3CH{=}CH_2$) = 20.4 kJ·mol^{-1} (ref 37) gave $\Delta H_f°([\mathbf{4}]^{\bullet+})$ = 545 ± 10 kJ·mol^{-1}, notably higher than the previous estimate[29] (vide infra). The thermochemical data for neutral and ionized enols **1–4** are summarized in Table II and complemented with the data for the lower homologues **5–8**.

Scheme III



Discussion

The thermochemical properties of simple enols can be discussed from different points of view. The enol can be regarded as a hydroxyl-substituted olefin[38] and the enthalpy change due to the substitution expressed by the heat of the isodesmic reaction (eq 3) in the gas phase (ΔH_r). Excluding ethenol, the evaluation of



$$(R^2)(R^3)C{=}C(R^1)(H) + CH_3OH \rightarrow (R^2)(R^3)C{=}C(R^1)(OH) + CH_4 \quad (3)$$

thermochemical data for 10 simple enols, dienols, and yne-enols[13b–j] gives an average value of ΔH_r = −68 ± 5 kJ·mol^{-1} (ref 39). The

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(30) Tureček, F.; Maquin, F.; Hill, N.; Stahl, D.; Gäumann, T. *Org. Mass Spectrom.* **1988**, *23*, 91.

(31) Vogt, J.; Pascual, C. *Int. J. Mass Spectrom. Ion Phys.* **1972**, *9*, 441.

(32) Levin, R. D.; Lias, S. G. *Ionization Potential and Appearance Potential Measurements 1971-1981*; NSRDS-NBS 71; U.S. Government Printing Office: Washington, DC, 1982.

(33) Friege, H.; Klessinger, M. *J. Chem. Res.* **1977**, 208.

(34) Hernandez, R.; Masclet, P.; Mouvier, G. *J. Electron Spectrosc. Relat. Phenom.* **1977**, *10*, 333.

(35) Tamm, W.-C.; Yee, D.; Brion, C. E. *J. Electron. Spectrosc. Relat. Phenom.* **1974**, *4*, 77.

(36) Holmes, J. L.; Lossing, F. P. *J. Am. Chem. Soc.* **1980**, *102*, 1591.

(37) Pedley, J. B.; Rylance, J. *Sussex N.P.L. Computer Analyzed Thermochemical Data; Organic and Organometallic Compounds*; University of Sussex: Sussex, 1977.

(38) Greenberg, A.; Stevenson, T. A. *J. Am. Chem. Soc.* **1985**, *107*, 3488.

(39) This holds for $\Delta H_r(3)$ = $\Delta H_f°$(products) − $\Delta H_f°$(reactants). The average ΔH_r reported previously (67 ± 7 kJ·mol^{-1})[13j] was an absolute value that included the term for ethenol.

Table III. MNDO Heats of Formation (kJ·mol^{-1}) and Net Atomic Charges for **1–4**

			net charge			
enol	isomer	$\Delta H_f°$	C(β)	C(α)	O	H(O)
1	syn	−216	−0.22	0.07	−0.26	0.19
	anti	−209	−0.15	0.03	−0.26	0.19
2	syn	−216	−0.22	0.07	−0.25	0.19
	anti	−213	−0.14	0.03	−0.26	0.19
3	syn	−213	−0.28	0.13	−0.26	0.20
	anti	−212	−0.21	0.09	−0.26	0.19
4	syn	−232	−0.26	0.09	−0.26	0.19
	anti	−229	−0.18	0.05	−0.26	0.19

ΔH_r calculated from the experimental heats of formation of **3** and **4** (Table II) are compatible with the above-average value and show that there are no unusual stabilizing or destabilizing factors in these enols. By contrast, the ΔH_r calculated for **1** and **2** on the basis of the reported[36] $\Delta H_f°([\mathbf{1}]^{\bullet+})$ (Table II, entries 1, 2, and values in parentheses) deviate significantly from the average in that they show a seemingly greater stabilization for the hydroxyl-substituted 2-butenes.

The gas-phase heats of formation of methyl-substituted enols **1–4** can be estimated from standard group equivalents, as implemented in Benson's rules,[9,14] and the term for the enolic hydroxy group.[13j] Within the limits of their applicability[9] the rules hold best for groups of closely related compounds. It has been noted[9] that for a compound within such a group a large discrepancy between the experimental $\Delta H_f°$, and the predicted one casts doubt on the accuracy of the former. The estimates for **3** and **4** (Table II) are in excellent agreement with the experimental values, as can be expected from the nondeviating ΔH_r in eq 3. However, for **1** and **2** the experimental $\Delta H_f°$ (values in parentheses, vide supra) are much lower than the estimates. This is surprising for compounds that are structurally related to the other, regularly behaving methylated enols, while not standing at the extremes of the series where some deviations could be anticipated (cf. the value for **5** in Table II).

In order to obtain an independent estimate, we calculated the $\Delta H_f°$ for the syn and anti rotational isomers of **1–4** using the MNDO method.[40] MNDO calculations of a number of simple enols have been shown earlier[13j] to be reliable in providing $\Delta H_f°$ values close to the experimental ones. The calculated $\Delta H_f°$ and atomic net charge populations are summarized in Table III. According to the calculations, there is no exceptional stabilization in **1** and **2** compared with the isomer **3**. Rotational syn isomers are calculated to be more stable than the corresponding anti isomers, in line with the syn preference found experimentally for the lower members of the series, **5** and **6**.[13d,41] Polarization of the enol system, expressed by net atomic charges at C(β), C(α), and the oxygen atom, has been correlated with the relative stabilities of simple enols.[42] The present calculations indicate that the net atomic charges are sensitive to the syn or anti geometry of the molecules, while there is no clear correlation between enol thermochemistry and the calculated charge distributions.

The experimental heats of formation of **1** and **2** are constructed from the ionic $\Delta H_f°$ and the ionization energies of neutral enols. The apparent overstabilization of **1** and **2** may thus be due to either the $\Delta H_f°([\mathbf{1}]^{\bullet+})$ being too low or the ionization energies being too high, or a combination of both. Perusal of the ionization energies of methyl-substituted enols shows that placing a methyl at the C(α) or C(β) position of the enolic double bond results in IE decrements of similar magnitude, as illustrated with the IE values of **6–8** relative to that of **5** (Table II). Hence, introduction into propenols of the second methyl at C(β) to give **3** or at C(α) to give **1** or **2** can be expected to have similar effects on the ionization energies. The experimental IE (Table II) are in full agreement with this prediction. By comparison, the IE decrease upon methyl substitution in enols, e.g. IE(**5**) − IE(**1**) = 0.74 eV, is comparable to that in closely related enol ethers, IE($CH_2{=}CHOCH_3$) − IE($CH_3CH{=}C(OCH_3)CH_3$) = 0.70 eV.[33] Furthermore, the ionization energies of enols **1–8** follow a nonlinear law given by eq 4, where n is the total number of atoms in the enol molecule.[43]

$$\text{IE (eV)} = 7.48 + 11.89/n \tag{4}$$

The fit is reasonably tight for **1–8** (standard deviation, s = 0.047 eV; correlation coefficient, r = 0.988) and shows no significant absolute deviations for the 2-buten-2-ols **1** and **2**. Hence, we believe that the experimental IE for **1** and **2** are not in gross error.

Substitution effects on the heats of formation of ionized enols have been evaluated experimentally[12] and interpreted by theory.[42] Introduction of a methyl at C(α) or C(β) in $[CH_2{=}CHOH]^{\bullet+}$ results in comparable decreases of the $\Delta H_f°$ of the isomeric ions (−96 and −92 kJ·mol^{-1} for $[\mathbf{6}]^{\bullet+}$ and $[\mathbf{8}]^{\bullet+}$, respectively; cf. Table II).[12] Introduction in $[\mathbf{6}]^{\bullet+}$ or $[\mathbf{7}]^{\bullet+}$ of the second methyl at C(β) to give $[\mathbf{3}]^{\bullet+}$ results in a smaller $\Delta H_f°$ decrement (−58 kJ·mol^{-1}).[12] This is in line with the rule[44] stating that the heats of formation of organic ions follow nonlinear laws in homologous series. Although enols $[\mathbf{3}]^{\bullet+}$ – $[\mathbf{8}]^{\bullet+}$ are not homologues in the strict sense of the word,[44] their $\Delta H_f°$ fit eq 5, where n is the total number of atoms in the ion.[44a]

$$\Delta H_f° \text{ (kJ·mol}^{-1}\text{)} = 648.8 - 11.446n + 1310.8/n \tag{5}$$

While the fit is very good for the above enol ions (s = 4.7 kJ·mol^{-1}, r = 0.999), the experimental $\Delta H_f°([\mathbf{1}, \mathbf{2}]^{\bullet+})$ deviates conspicuously from the value calculated from eq 5 (601 kJ·mol^{-1}). The cause for such a large deviation is not clear.[45] By comparison, the heats of formation of cation radicals derived from methyl-subsituted benzenes[44a] and, especially, alkenes whose thermochemistry is analogous to that of ionized enols as far as substituent effects are concerned,[46] can be fitted into formulas of the type (5).[47] In the latter series there are no deviations for the 2-butene system. We conclude that the reported $\Delta H_f°([\mathbf{1}, \mathbf{2}]^{\bullet+})$[12] is perhaps too low to be compatible with the thermochemical data of the series of ionized and neutral enols. Hence, we prefer using the value interpolated from eq 5: $\Delta H_f°([\mathbf{1}, \mathbf{2}]^{\bullet+}$ = 601 kJ·mol^{-1}.

Another criterion for discussing enol thermochemistry is based on the comparison of the *relative* enol–oxo stabilities given by $\Delta H_f°$(enol–oxo) = $\Delta H_f°$(enol) − $\Delta H_f°$(oxo). Within a series of related compounds these relative stabilities express only the differences in the substituent effects on the enols and their oxo counterparts, and, by this virtue, they are less straightforward than the $\Delta H_f°$ values themselves. Nevertheless, the experimental $\Delta H_f°$(enol–oxo) may provide a reference basis for theoretical calculations of the relative stabilities of **1–4** that are within reach of the current sophisticated ab initio methods.[42b]

The $\Delta H_f°$(enol–oxo) data (Table II) clearly show that the enols fall into two series, i.e. the aldehyde enols and the ketone enols. Out of these two series, the aldehyde enols are in general less destabilized against the corresponding aldehydes, and the $\Delta H_f°$(enol–oxo) values further decrease with the increasing number of methyl groups at C(β). The stabilizing effect of the C(β) methyls is also observable with the ketone enols (Table II). These β-effects are of comparable magnitude in both series and amount to −14.5 ± 4 and −14 ± 5 kJ·mol^{-1} for the aldehyde and

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(40) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899.

(41) (a) Rodler, M.; Bauder, A. *J. Am. Chem. Soc.* **1984**, *106*, 4025. (b) Capon, B.; Siddhanta, A. K. *J. Org. Chem.* **1984**, *49*, 255.

(42) (a) Frenking, G.; Heinrich, N.; Schmidt, J.; Schwarz, H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1982**, *37*, 1597. (b) Heinrich, N.; Koch, W.; Frenking, G.; Schwarz, H. *J. Am. Chem. Soc.* **1986**, *108*, 593.

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

(44) (a) Holmes, J. L.; Fingas, M.; Lossing, F. P. *Can. J. Chem.* **1981**, *59*, 80. (b) Holmes, J. L.; Lossing, F. P. *Can. J. Chem.* **1982**, *60*, 2365.

(45) Professor Holmes and Dr. Lossing have informed us that they were able to reproduce their previous measurements[36] of AE($[\mathbf{1}, \mathbf{2}]^{\bullet+}$) within 0.02 eV.

(46) Terlouw, J. K.; Heerma, W.; Holmes, J. L.; Burgers, P. C. *Org. Mass Spectrom.* **1980**, *15*, 582.

(47) Alkene cation radicals in the series ethene, propene, 2-butenes, 2-methylpropene, 2-methyl-2-butene, and 2,3-dimethyl-2-butene fit the formula $\Delta H_f°$ (kJ·mol^{-1}) = 1031.3 − 19.778n + 925/n, with s = 3.0 kJ·mol^{-1} and r = 0.9997.

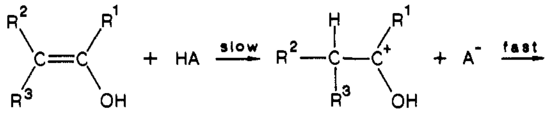
Table IV. Estimated Proton Affinities of Unstable Enols[a]

			proton affinity, $kJ \cdot mol^{-1}$	
entry	enol	oxo form	oxo[a]	enol
1	$CH_2{=}CHOH$	CH_3CHO	781	819
2	(*E*)-$CH_3CH{=}CHOH$	CH_3CH_2CHO	793	816
3	(*Z*)-$CH_3CH{=}CHOH$	CH_3CH_2CHO	793	811
4	$(CH_3)_2C{=}CHOH$	$(CH_3)_2CHCHO$	806	815
5	(*E*)-$CH_2{=}CHCH{=}CHOH$	$CH_3CH{=}CHCHO$	835.5	849[b]
		$CH_2{=}CHCH_2CHO$	<800[c]	<789[b]
6	(*Z*)-$CH_2{=}CHCH{=}CHOH$	$CH_3CH{=}CHCHO$	835.5	851[b]
		$CH_2{=}CHCH_2CHO$	<800[c]	<791[b]
7	$CH_2{=}C(OH)CH_3$	CH_3COCH_3	823	864, 870[d]
8	$CH_2{=}C(OH)CH_2CH_3$	$CH_3COCH_2CH_3$	836	881[e]
9	(*E*)-$CH_3CH{=}C(OH)CH_3$	$CH_3COCH_2CH_3$	836	865
10	(*Z*)-$CH_3CH{=}C(OH)CH_3$	$CH_3COCH_2CH_3$	836	863
11	$(CH_3)_2C{=}C(OH)CH_3$	$CH_3COCH(CH_3)_2$	841	862
12	$CH_2{=}CHC(OH){=}CH_2$	$CH_3COCH{=}CH_2$	838	873[f]
13	$CH_2{=}C(OH)Ph$	$PhCOCH_3$	859	900[g]

[a] Values from ref 51. [b] Based on the $\Delta H_f°$ from ref 13g. PA((*Z*)-2-butenal) was taken equal to that of the *E* isomer. [c] Estimated from the proton affinity of 1-butanal. [d] Based on thd $\Delta H_f°$ from ref 13c and ref 13i, respectively. [e] Based on $\Delta H_f°(CH_2{=}C(OH)CH_2CH_3) = -196\ kJ \cdot mol^{-1}$.[13i] [f] Based on the $\Delta H_f°$ from ref 13e. [g] Based on the $\Delta H_f°$ from ref 13h.

ketone enols, respectively. It should be noted that the β-effect need not be particular to the enol system only. For instance, simple alkenes show a similar trend in that a substitution by methyl at an sp^2-carbon atom provides better stabilization than does a substitution at an sp^3-carbon.[48] In contrast to this, methyl substituents at C(α) make the $\Delta H_f°$(enol–oxo) larger by $8 \pm 3\ kJ \cdot mol^{-1}$. This α-effect indicates that the carbonyl group in general gains better stabilization than does the enol system when a methyl group is placed at the electron-deficient oxygen-bearing carbon atom.

Proton Affinities and Surface-Catalyzed Isomerization of Enols. The substituents at C(α) and C(β) in the enol system have great impact on the kinetics of enol–oxo isomerization. It has repeatedly been observed that aldehyde enols isomerize much slower than do ketone enols, regardless of the surrounding medium. For instance, the half-lives of the aldehyde enols **3** and **5–7** in hexane solution at 3 °C range from several minutes to 10 h, while ketone enols isomerize too fast to be followed by classical spectroscopic methods.[7] The mechanism of the tautomerization has been elucidated by Kresge and co-workers.[21] The isomerization is initiated by protonation at C(β) of the enol double bond followed by abstraction of the hydroxyl proton (eq 6) to give the oxo form. The first step is slow and rate-determining, while the deprotonation is fast.[21]



(6)

When the enol is generated at 10^{-6} Torr by flash-vacuum pyrolysis, intermolecular collisions are so rare that an isomerization induced by a gaseous acid, e.g. residual water or the enol itself, is practically excluded. Further, the internal energy of the enol molecules coming out of the hot zone is insufficient to bring about unimolecular enol–oxo isomerization, which is symmetry-forbidden and has a high activation energy.[13g,49] The isomerization can proceed on the surface of the ionization chamber where the enol molecules undergo on average of 100 wall collisions before they are ionized or pumped out. The metallic surface contains catalytically active centers or areas formed by oxidation and subsequent hydration of metal oxides and doped by organic decomposition products due to ion source conditioning. The surface need not be homogeneous and is likely to contain catalytical centers of different activities that can induce acidic–basic isomerizations. According to eq 6 the enol–oxo isomerization will occur if the catalytically active center is able to protonate the enol within the time of adsorption–desorption. Under our experimental conditions [100 °C (10^{-6} Torr), scan rates of a few seconds per peak] more than 90% of the ion source inner surface is hit by the gaseous molecules during the time of measurement. The acidic–basic centers on the surface are therefore scanned at random by the colliding enol molecules. The conversion rate, enol → oxo, will depend on the fraction of catalytic centers being present that can protonate the enol of a given basicity at the given ion source temperature. Hence, the basicities may provide a guide for the qualitative assessment of the propensities of enols toward isomerization. Enol basicities in the interaction with acidic–basic surfaces are unknown but can be approximated by the corresponding gas-phase proton affinities (PA), which are related to gas-phase basicities.[50] As protonation of the enol and its oxo counterpart produces the same ion (eq 6), it holds that

$$PA(enol) = PA(oxo) + \Delta H_f°(enol) - \Delta H_f°(oxo) \quad (7)$$

Equation 7 makes it possible to evaluate proton affinities for unstable enols with the tabulated PA values of aldehydes and ketones[51] and the $\Delta H_f°$(enol–oxo)[13j] (Table IV).[52,53]

According to Table IV there are quantitative differences between the PA of aldehyde enols on the one hand and those of ketone enols on the other. Simple aldehyde enols (Table IV, entries 1–4) show in general *lower proton affinities* than do the ketone enols. Turning back to the surface-catalyzed isomerization, for a surface of the given distribution of acidic centers there will be a smaller fraction of those that can induce the isomerization of aldehyde enols compared with ketone enols, and consequently the isomerization of the former will be less frequent, i.e. slower.

Structurewise there are several interesting features revealed by the PA values.

First, methyl substituents at C(β) have a negligible effect on the enol proton affinities within the accuracy of the present estimates. This holds for both the aldehyde (Table IV, entries 1–4)

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(48) (a) Pross, A.; Radom, L. *Prog. Phys. Org. Chem.* **1981**, *13*, 1. (b) Topsom, R. D. *Acc. Chem. Res.* **1983**, *16*, 292. (c) Hine, J.; Skoglund, M. J. *J. Org. Chem.* **1982**, *47*, 4766. (d) Apeloig, Y.; Karni, M. *J. Am. Chem. Soc.* **1984**, *106*, 6676.

(49) Bouma, W. J.; Poppinger, D.; Radom, L. *J. Am. Chem. Soc.* **1977**, *99*, 6443.

(50) Aue, D. H.; Bowers, M. T. In *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic: New York, 1979; Chapter 9.

(51) Lias, S. G.; Liebman, J. F.; Levin, R. D. *J. Phys. Chem. Ref. Data* **1984**, *13*, 695.

(52) Protonation of the enol system at centers other than C(β) is likely to be less exothermic. For instance, ion $CH_2{=}CHOH_2^+$ due to protonation of the hydroxy group in **5** is substantially less stable than $CH_3CH{=}OH^+$ due to protonation at C(β).[53] Protonation at C(α) is energetically disadvantageous, as the corresponding olefins have substantially lower proton affinities than the enols.[51,54] Compound **3** may be an exception, as the stabilities of $(CH_3)_2C^+CH_2OH$ and $(CH_3)_2CHCH{=}OH^+$ can be comparable.[51]

(53) (a) Nobes, R. H.; Rodwell, W. R.; Bouma, W. J.; Radom, L. *J. Am. Chem. Soc.* **1981**, *103*, 1913. (b) Nobes, R. H.; Radom, L. *Chem. Phys. Lett.* **1983**, *99*, 107. (c) Keyes, B. G.; Harrison, A. G. *Org. Mass Spectrom.* **1974**, *9*, 221. (d) Burgers, P. C.; Terlouw, J. K.; Holmes, J. L. *Org. Mass Spectrom.* **1982**, *17*, 369.

and the ketone (entries 7–11) series of enols. The insensitivity of the enol PA toward alkyl substitution at C(β) suggests that the stabilizing effects exerted by the β-methyls are of comparable magnitude in neutral and protonated enols. Similar situation has been encountered with 2,3-dihydrofurans in which a β-methyl group does not increase the basicity of the enol ether moiety.[54] However, in contrast to this, ethyl 1-propenyl ether has been found to be more basic[54] than ethyl vinyl ether, so the β-methyl effect on the proton affinity may be particular to the molecular system in question.

Second, protonation of the polarizable 1-hydroxybutadiene system (Table IV, entries 5 and 6) will proceed preferentially in the terminal position (C-4) to give 2-butenal. The proton affinities estimated for 1-hydroxybutadienes are notably higher than those for simple aliphatic aldehyde enols. This explains why 1-hydroxybutadienes are rather sensitive to surface-catalyzed isomerization to 2-butenal despite that their $\Delta H_f°$(enol–oxo) values match those of simple aldehyde enols.[13g]

Third, α-substituents exert pronounced effects on the proton affinities of ketone enols. Referred to ethenol, introduction at C(α) of σ-donors (Table IV, entries 7 and 8) or π-donors (entries 12 and 13) greatly increases the proton affinity of the resulting ketone enol. The considerable difficulties in the preparation of pure gaseous ketone enols (refs 13c,e,h,i) can therefore be attributed to the high basicity of these compounds that makes them prone to acid-catalyzed isomerization.

Conclusions

The gas-phase heats of formation of methyl-substituted neutral and ionic enols can be fitted into self-consistent empirical formulae. Ionic heats of formation follow the nonlinear law expressed by eq 5. The heats of formation of neutral enols can be reliably estimated from standard hydrocarbon groups equivalents[14] supplemented with the term for the enolic hydroxy group.[13j] The enol stabilities, relative to their oxo counterparts, depend on the position of the substituent. Methyl groups at C(β) tend to stabilize the enols by 14 kJ·mol^{-1}. Methyl groups at C(α) destabilize the enols relative to the corresponding ketones by 8 kJ·mol^{-1}. Gas-phase proton affinities have been estimated from the thermochemical data and shown to be related to the enol kinetic stabilities. Simple aldehyde enols display relatively low proton affinities that are remarkably insensitive to the presence of β-methyl substituents (PA = 815 ± 3 kJ·mol^{-1}). The proton affinities of the ketone enols range within 862-900 kJ·mol^{-1}, strongly depending on the nature of the C(α) substituent. β-Methyl substituents have negligible effect on the proton affinities of ketone enols.

Experimental Part

Methods. Mass spectra were measured on a JEOL D-100 double-focusing instrument (50 μA, 75 eV, 3 kV) equipped with a molecular flow microoven.[13a] The temperature of the ion source was kept at 90–100 °C as read with a chromel–alumel thermometer without applying high voltage to suppress charging effects. The ionization and appearance energies were measured with the repeller voltage set to 0.00 ± 0.02 V. Ion intensities were recorded with a data system at a slow scan rate (60 min/mass decade) in 50-meV steps starting from ca. 0.5 eV below the threshold up to 1–3 eV above it. The intensities were averaged over three to four scans at each electron energy, normalized, and then treated with the inverse-convolution procedure.[31] The reported energies are averages of five to seven independent runs. The energy scale was calibrated with methyl iodide (IE = 9.545 eV) as internal standard at the beginning, in the middle, and at the end of each 1-day measurement. The reported error limits are standard deviations including those of the energy calibration. ^{1}H NMR spectra were measured on a Varian XL-200 instrument (200.058 MHz, Fourier transform mode) in $CDCl_3$ at 23 °C with tetramethylsilane as internal standard.

Materials. 3-*exo*-Methylbicyclo[2.2.1]hept-5-en-2-ol (**10**) was prepared from bicyclo[2.2.1]hept-5-en-2-one (**9**) as described previously.[25]

2-*exo*,3-*exo*- and 2-*endo*,3-*exo*-Dimethylbicyclo[2.2.1]hept-5-en-2-ol (11, 12). Ketone **10** (1 g, 8.2 mmol) in dry ether (20 mL) was added at 0 °C to a solution of methylmagnesium iodide (12 mmol) in ether. After being stirred at 0 °C for 2 h, the reaction was quenched with aqueous ammonium chloride, the ethereal layer was separated, washed with aqueous sodium thiosulfate, and dried over sodium sulfate, and ether was removed on a rotatory evaporator. The residue was chromatographed on silica gel (elution with pentane–ether, 3:1) to give **11** (R_f 0.52; 590 mg, 52%), **12** (R_f 0.38; 210 mg, 19%), and a fraction (120 mg, 11%) containing **11**, **12**, and another isomer. Alcohols **11** and **12** were further purified by short-path vacuum distillation at 90–100 °C (12 Torr).

11. Anal. Found: C, 78.16; H, 10.28. Calcd: C, 78.21; H, 10.21. ^{1}H NMR: 6.20 (dddd, J = 5.6, 3.0, 0.6, 0.6 Hz, H-6), 6.04 (dddd, J = 5.6, 3.0, 0.6, 0.6 Hz, H-5), 2.49 (m, w = 8 Hz, H-1), 2.38 (m, w = 9 Hz, H-4), 1.95 (m, J = 8.7, 1.5, 1.5, 0.6, 0.6 Hz, H-7-anti), 1.47 (dm, J_d = 8.7 Hz, H-7-syn), 1.38 (dq, J_q = 7 Hz, J_d = 2.1 Hz, H-3-endo), 1.17 (s, 3 H), 1.01 (d, J = 7.1 Hz, 3 H). Mass spectrum: $M^{\bullet+}$, m/z 138 (found 138.1052, $C_9H_{14}O$ requires 138.1044).

12. Anal. Found: C, 78.32; H, 10.16. Calcd: C, 78.21; H, 10.21. ^{1}H NMR: 6.47 (ddm, J = 5.6, 3.0 Hz, H-6), 6.17 (ddm, J = 5.6, 3.0 Hz, H-5), 2.59 (m, w = 9 Hz, H-1), 2.42 (m, w = 9 Hz, H-4), 1.61 (dm, J_d = 9.2 Hz, H-7-anti), 1.50 (dm, J_d = 9.2 Hz, H-7-syn), 1.33 (s, H-3), 1.31 (dq, J_q = 7 Hz, J_d = 2.1 Hz, H-3-endo), 1.05 (d, J = 7 Hz, 3 H).

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(54) Bouchoux, G.; Djazi, F.; Hoppilliard, Y.; Houriet, R.; Rolli, E. *Org. Mass Spectrom.* **1986**, *21*, 209.