(*E*)- and (*Z*)-Prop-1-en-1-ol: Gas-phase Generation and Determination of Heats of Formation by Mass Spectrometry

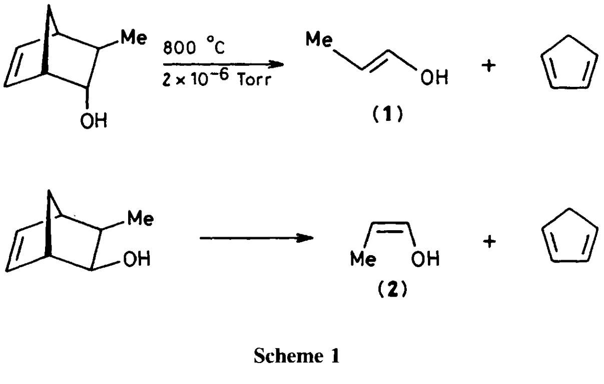
František Tureček

The Jaroslav Heyrovský Institute of Physical Chemistry and Electrochemistry, Máchova 7, 121 38 Praha 2, Czechoslovakia

The unstable (*E*)- and (*Z*)-prop-1-en-1-ol were generated in the gas phase and their heats of formation determined as −169 to −174 kJ mol^{-1}.

Enol forms of simple aldehydes and ketones are usually less stable than the corresponding oxo forms.[1] Although simple enols can be generated as transient species in solution and characterized by spectral data,[2] their fundamental thermochemical properties are mostly obtained from gas-phase studies[3] or theoretical calculations.[4]

The system prop-1-en-1-ol–propanal involves another kind of isomerism, in addition to keto–enol tautomerism, as the enol form can exist as an (*E*)- or (*Z*)-isomer. In this work we have generated the isomeric (*E*)- and (*Z*)-prop-1-en-1-ols (**1**) and (**2**), respectively, by retro-Diels–Alder reaction of the corresponding 3-methylnorborn-5-en-2-ols (Scheme 1) by high-vacuum flash pyrolysis.[3] The products were cooled to 150 °C within one millisecond after their formation by



Scheme 1

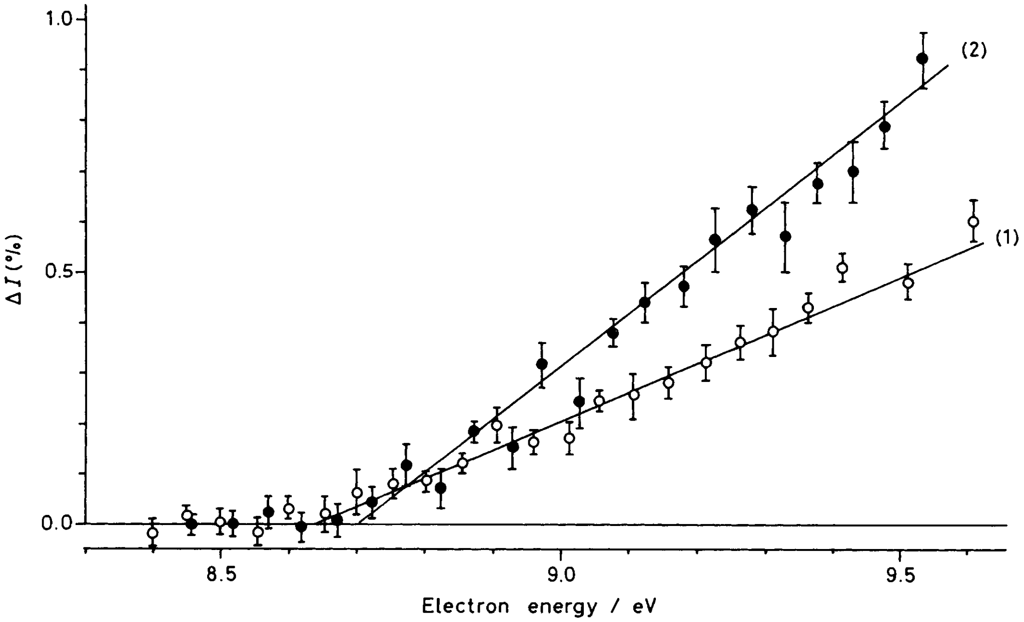


Figure 1. Deconvoluted ionization efficiency curves for (**1**), ○; (**2**), ●.

collisions with the walls of an ion source, and then analysed by electron-impact mass spectrometry.

The 75 eV mass spectra of (**1**) and (**2**)† differ significantly from those of other C_3H_6O isomers[5] and, to some extent, from each other as well. The ionization energies of (**1**) and (**2**) were determined as 8.64 ± 0.02 and 8.70 ± 0.03 eV, respectively (measured with inverse convolution of the electron energy[6]). These data, combined with the heat of formation of ionized prop-1-en-1-ol ($\Delta H^\circ_{f,298}$ 665 kJ mol^{-1}, geometry unspecified[7]), give $\Delta H^\circ_{f,298}$ (**1**,**2**) = −169 to −174 kJ mol^{-1}. Hence the isomeric prop-1-en-1-ols are 17—22 kJ mol^{-1} less stable than propanal ($\Delta H^\circ_{f,298}$ −191 kJ mol^{-1})[8] and they would exist in negligible amounts in a keto–enol equilibrium mixture.

The question of the relative stability of (**1**) and (**2**) cannot be definitely answered at the present level of accuracy of the ΔH_f data. *Ab initio* calculations[9] suggest that the (*Z*)-ion $(\mathbf{2})^{\cdot+}$ is *ca.* 2 kJ mol^{-1} more stable than the (*E*)-isomer $(\mathbf{1})^{\cdot+}$. As the (*Z*)-isomer (**2**) has a higher ionization potential than (**1**), the former would be expected to be more stable. Nevertheless, the $\Delta H^\circ_{f,298}$ values obtained from theoretical calculations [676 and 674 kJ mol^{-1} for $(\mathbf{1})^{\cdot+}$ and $(\mathbf{2})^{\cdot+}$, respectively, referred to the experimental $\Delta H^\circ_{f,298}$ of prop-1-en-2-ol cation radical[7]] exceed the experimental $\Delta H^\circ_{f,298}$ of ionized prop-1-en-1-ol and thus do not provide a firm basis for estimating the ΔH_f of the neutral enols. By comparison, with closely related (*E*)- and (*Z*)-1-alkoxypropenes, RO–CH=CH–CH_3, the (*E*)- isomer is more stable for R = Me, but less stable for R = Bu^t,[10] though the situation is complicated by the existence of rotamers.

The population of rotamers (*s-cis vs. s-trans*) in (**1**) and (**2**) can be assessed on the basis of the ionization efficiency curves (Figure 1). The curve for (**2**) clearly shows a steeper slope near the threshold than does that of (**1**), which indicates different Franck–Condon factors in ionization of the isomers. Theoretical and spectral data[11] for the closely related ethenol suggest that the *s-cis* conformation is preferred in the neutral enols. By analogy, (**1**) may exist in a more stable *s-cis* form in contrast to the ion $(\mathbf{1})^{\cdot+}$ which should prefer the *s-trans* geometry.[9] Assuming that the population of rotamers in (**1**) is similar to that in ethenol, where the energy difference between the *s-trans* and *s-cis* forms was calculated as 7 kJ mol^{-1},[11] about 12% of the less stable *s-trans* form of (**1**) would be present at 150 °C (entropy term neglected), and this will result in a lowered probability of ionization, as also reported for ethenol.[3]

In the (*Z*)-isomer (**2**), however, the *s-cis* form cannot be significantly populated owing to steric repulsion of the methyl group with the hydroxy hydrogen atom (the van der Waals radii overlap on molecular models).[10] Since only the planar *s-trans* forms would be stable in this case,[11] the molecular geometries of (**2**) and $(\mathbf{2})^{\cdot+}$ can correlate, making the ionization more probable than in (**1**).

Received, 29th June 1984; Com. 925

References

1 H. Hart, *Chem. Rev.*, 1979, **79**, 515.
2 B. Capon, D. S. Rycroft, T. W. Watson, and C. Zucco, *J. Am. Chem. Soc.*, 1981, **103**, 1761.
3 J. L. Holmes and F. P. Lossing, *J. Am. Chem. Soc.*, 1982, **104**, 2648; F. Tureček and V. Hanuš, *Org. Mass Spectrom.*, 1984, **19**, in the press.
4 W. J. Bouma, L. Radom, and W. R. Rodwell, *Theor. Chim. Acta*, 1980, **56**, 149.
5 F. Tureček and V. Hanuš, *Org. Mass Spectrom.*, 1984, **19**, in the press.
6 J. Vogt and C. Pascual, *Int. J. Mass Spectrom. Ion Phys.*, 1972, **9**, 441.
7 J. L. Holmes and F. P. Lossing, *J. Am. Chem. Soc.*, 1980, **102**, 1591.
8 S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw, and R. Walsh, *Chem. Rev.*, 1969, **69**, 279.
9 W. J. Bouma, J. K. MacLeod, and L. Radom, *J. Am. Chem. Soc.*, 1981, **102**, 2246.
10 T. Okuyama, T. Fueno, and J. Furukawa, *Tetrahedron*, 1969, **25**, 5409.
11 R. H. Nobes, L. Radom, and N. L. Allinger, *J. Mol. Struct. (THEOCHEM)*, 1981, **85**, 185.

---

† 75 eV Mass spectra of (**1**) and (**2**) (*m/z*, rel. intensity): (**1**), 58(100), 57(67), 56(3), 55(8), 43(51), 42(6), 41(37), 40(10), 39(59), 38(11), 37(7), 31(38), 30(8), 29(92), 28(41), 27(100), 26(37), 25(7), 15(28), and 14(11); (**2**), 58(77), 57(63), 56(5), 55(7), 43(56), 42(7), 41(42), 40(12), 39(71), 38(18), 37(9), 31(40), 30(9), 29(100), 28(55), 27(100), 26(34), 25(6), 15(42), and 14(11). The relative intensities of ions at *m/z* 41, 40, 39, 38, 37, 27, 26, 25, and 14 were corrected for contributions from cyclopentadiene.