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2-HYDROXYBUTADIENE: PREPARATION, IONIZATION ENERGY AND HEAT OF FORMATION

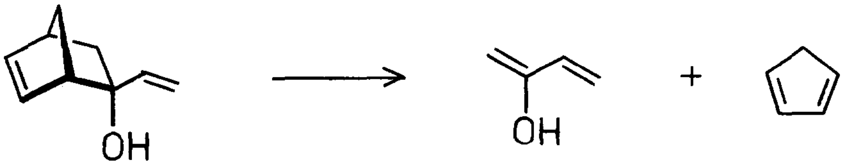
František TUREČEK

J. Heyrovský Institute of Physical Chemistry and Electrochemistry
Máchova 7, 121 38 Praha 2, Czechoslovakia

Summary: 2-Hydroxybutadiene was generated in the gas phase and its heat of formation determined as -77 ± 5 kJ/mol.

Butadienes containing OR, OAc or $OSiR_3$ groups are useful four-carbon synthons, and their preparation and reactivity has been given much attention.[1] By contrast, the parent hydroxybutadienes represent elusive enol-forms of the more stable unsaturated aldehydes or ketones and their basic properties have been unknown. 2-Hydroxybutadiene has been prepared as an air-sensitive iron-tricarbonyl complex and characterized through its ^1H-NMR spectrum.[2] The present letter reports on the preparation of free 2-hydroxybutadiene(1) in the gas phase and determination of its ionization energy (IE) and heat of formation ($\Delta H^o_{f,298}$).

The unstable enol 1 was generated by the retro-Diels-Alder reaction of 5-*exo*-vinyl-5-norbornenol (2)[3] under conditions of high-vacuum flash pyrolysis at 800 °C/ 2.10^{-6} Torr.



2 1

Molecules of the precursor 2 were allowed to undergo ca. 30 collisions with the hot walls of a micro-oven[4] and then decomposed to 1 and cyclopentadiene within 1 msec. The products were immediately cooled to 150 °C by collisions with the walls of an ion source and analyzed by mass spectrometry. The 75 eV mass spectrum of 1[5] differs from those of stable C_4H_6O isomers with a C-C-C(O)-C, C-C-C-C-O or cyclic frame.[6] The ionization energy of 1 was determined from a deconvoluted ionization efficiency curve[7] as IE = 8.68 ± 0.03 eV. There is a second onset at 9.65 eV which coincides with the IE of methylvinylketone (3)(IE = 9.64 eV).[8] The latter oxo-form is probably formed by surface-catalysed isomerization of 1 in an amount estimated as 20-30%. It is worth noting that simple enol-forms of the type R-C(OH)=CH_2 (R = CH_3, -CH=CH_2) appear to be more sensitive to enol-keto isomerization than enols bearing the hydroxy group at the terminal carbon atom, R-CH=CH-OH (R = H, CH_3).[4,9]

The value of IE(**1**), combined with the heat of formation of the ion $\mathbf{1}^{+\cdot}$ ($\Delta H^{o}_{f,298}$= 761 kJ/mol) (ref.[8]), gives us an estimate of $\Delta H^{o}_{f,298}(\mathbf{1})$ = -77 $\pm$ 5 kJ/mol. This means that the enol **1** is ca. 35 kJ/mol less stable than its keto-form **3** ($\Delta H^{o}_{f,298}$ =-112 kJ/mol).[10] The difference in the $\Delta H^{o}_{f,298}$ between **1** and **3** is slightly lower than that found for a simpler system 2-propenol-acetone ($\Delta\Delta H^{o}_{f,298}$= 42 kJ/mol).[9a]

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