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1-PHENYLETHENOL: THE ENOL FORM OF ACETOPHENONE. PREPARATION, IONIZATION ENERGY AND THE HEAT OF FORMATION IN THE GAS PHASE

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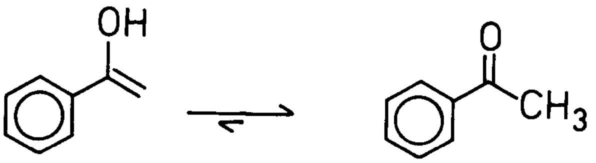
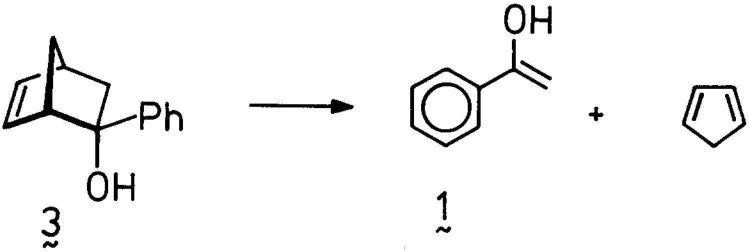
Summary: The enol form of acetophenone was generated in the gas phase and its ionization energy was determined as 8.01 ± 0.03 eV. The heat of formation of the enol was assessed as -46 ± 6 kJ.mol^{-1}. The enol is destabilized against acetophenone by 41 kJ.mol^{-1}.

1-Phenylethenol (1) was first detected in photoinduced enolization of acetophenone (2).[1] In a more recent study,[2] 1 was generated in solution by Norrish-II photofragmentation of butyrophenone and its pK_a was determined.[2] While 1 is undoubtedly less stable than 2, and isomerizes rapidly to the keto form upon acidobasic catalysis,[1] the corresponding ΔG and ΔH values for the enol-keto equilibrium have been the subject of argument.[3-5] Recent halometric determination of the equilibrium constant, K_e = [1]/[2] = 7.10^{-9}, implied ΔG(enol-keto) = -46.5 kJ.mol^{-1} in very dilute aqueous solution.[4] By contrast, thermochemical measurements,[3] based on enol ether hydrolysis,[6] yielded a value of ΔG = -38.2 kJ.mol^{-1}.[3] In the latter measurements, the final free enthalpy difference is obtained by combining thermochemical data pertinent to both the gas and liquid phase,[3] and corrections are necessary to make the data compatible with the experimental heat of hydrolysis in dilute aqueous solution.[3,6] Therefore, it became of interest to prepare enol 1 in the gas phase and determine its heat of formation by an independent method.



1 2

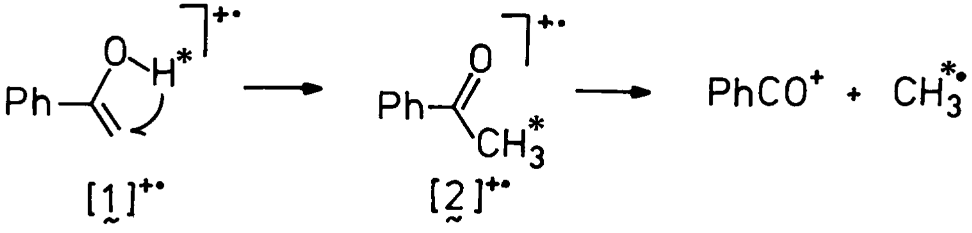
Kinetically unstable enols can be generated by the retro-Diels-Alder decomposition of suitable norbornene precursors by flash vacuum pyrolysis.[7] 2-*exo*-Phenylbicyclo[2.2.1]-hept-5-en-2-ol (3)[8] was found to smoothly decompose at 770-800°C and 2.10^{-6} Torr in a molecular-flow micro-oven coupled to a mass spectrometer[10] (Scheme 1).



Scheme 1

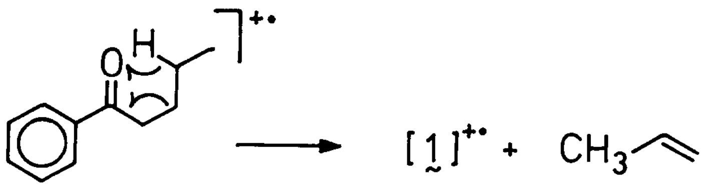
The C_8H_8O product (1) was characterized through its 75 eV electron impact mass spectrum[11] which was significantly different from that of 2.[12] Namely, 1 gives more abundant molecular ion than does 2, in keeping with the higher thermodynamic stability of ionized enols compared with the corresponding ionized oxo-forms.[13] The ionization efficiency curve of $(C_8H_8O)^{+\cdot}$ shows a break at 9.3 eV which coincides with the ionization energy of 2.[14] This indicates the presence of 2 in the pyrolysate in an amount estimated as 20-30%. Labelled analogues $[\text{O-}^2\text{H}]$-1 and $[(\text{E})\text{-2-}^2\text{H}]$-1 were prepared from the corresponding precursors, $[\text{O-}^2\text{H}]$-3 and [3-*exo*-^{2}H]-3, respectively.

Following electron impact ionization, $(1)^{+\cdot}$ undergoes loss of a methyl group to give $C_7H_7O^+$ fragments at *m/z* 105.[11] The mechanism of this reaction was investigated with the use of the labelled derivatives. In each case, deuterium was cleanly lost in the methyl eliminated. This shows that the formation of $C_7H_7O^+$ is not preceded by hydrogen exchange between the enol system and the aromatic ring. The loss of methyl can be viewed as proceeding via 1,3-hydrogen migration from the hydroxyl onto the methylene group, followed by decomposition of the intermediate ketone $(2)^{+\cdot}$ (Scheme 2).



Scheme 2

In order to assess $\Delta H_f^o(1)$ we determined the heat formation of the ionized enol $(1)^{+\cdot}$ and the threshold ionization energy (IE) of neutral 1. The former quantity followed from appearance energy (AE) measurements of $(1)^{+\cdot}$ prepared by the McLafferty rearrangement[15] in ionized valerophenone $(4)^{+\cdot}$ (Scheme 3).



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Scheme 3

The experimental appearance energy (AE = 9.31 ± 0.05 eV), combined with $\Delta H_f^o(4)$ (-149 kJ.mol^{-1})[16] and ΔH_f^o(propene) (20.4 kJ.mol^{-1})[16], gives $\Delta H_f^o(1)^{+\cdot}$ = 729 kJ.mol^{-1}. This is in fair agreement with an earlier measurement of AE$(1)^{+\cdot}$ from metastable molecular ions of butyrophenone,[18] whence $\Delta H_f^o(1)^{+\cdot}$ = 724 kJ.mol^{-1} can be deduced. The ionization energy of 1 was measured as IE = 8.01 ± 0.03 eV by the inverse convolution method.[19] Combination of the IE(1) and an average $\Delta H_f^o(1)^{+\cdot}$ (726 kJ.mol^{-1}) affords $\Delta H_f^o(1)$ = -46 ± 6 kJ.mol^{-1}. Hence, enol 1 is found to be 41 kJ.mol^{-1} less stable than the keto form 2.[17]

To compare the present data with those from calorimetric measurements,[3] it is necessary to transfer the latter to the gas phase. Hydrolysis and isomerization in the gas phase

$$\text{Ph-C(OCH}_3\text{)=CH}_2 + \text{H}_2\text{O} \rightarrow 1 + \text{CH}_3\text{OH} \rightarrow 2 + \text{CH}_3\text{OH}$$

requires ΔH_{tot} = -33 kJ.mol^{-1}, as calculated from the reaction enthalpy in the liquid phase[3] and the reported heats of vaporization.[3] The crucial point is to estimate the ΔH_{hyd} in the first step, $\text{Ph-C(OCH}_3\text{)=CH}_2 \rightarrow 1$, which is inaccessible by direct measurement.[6] Previous estimates, ranging from near thermoneutrality[20] up to +22 kJ.mol^{-1},[6] lead to ΔH_f^o(enol-keto) = $\Delta H_{tot} - \Delta H_{hyd}$ = -33 to -55 kJ.mol^{-1}. Our value (-41 kJ.mol^{-1}) falls within this interval, suggesting that neither method is in gross error. Nevertheless, the uncertainty in the enthalpy of enol ether hydrolysis is rather high. This can be amended by implementing ΔH_{hyd} values calculated for gas phase reactions[21]

$$\text{CH}_3\text{-C(OCH}_3\text{)=CH}_2 + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{-C(OH)=CH}_2 + \text{CH}_3\text{OH} \qquad (\Delta H_{hyd} = 11 \text{ kJ.mol}^{-1})$$

$$\text{(E)-CH}_3\text{-CH=CH-OCH}_3 + \text{H}_2\text{O} \rightarrow \text{(E)-CH}_3\text{-CH=CH-OH} + \text{CH}_3\text{OH} \qquad (\Delta H_{hyd} = 12 \text{ kJ.mol}^{-1})$$

The average value of ΔH_{hyd} combined with ΔH_{tot}[3] gives ΔH_f^o(enol-keto) = -44.5 kJ.mol^{-1} in good agreement with our value determined in the gas phase.

We conclude that the present data lend support to the results of thermochemical measurements in solution.[3]

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