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Enolization of Gaseous Acetone Radical Cations: Catalysis by a Single Base Molecule

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It is well-known that simple neutral enols are thermodynamically less stable than their keto isomers.[1] For example, experiments in the gas-phase show that the enol of acetone is 14 ± 2 kcal/mol[2] less stable than acetone itself, in agreement with ab initio calculations.[3] In solution, ketonization can be catalyzed by either acid or base and thus, enols are usually present in very low concentrations.

Upon one-electron oxidation a reversal of stability takes effect;[4] that is, for radical cations it is usually the enol form which is the more stable isomer. For example, experiments show that the gaseous acetone radical cation is 14 kcal/mol[5] *less* stable than its enol isomer, paralleling observations from theory.[3a,6] For the solitary ions a large barrier (37 kcal/mol[7]) for the 1,3-hydrogen shift prevents enolization, and thus once formed, acetone radical cations retain their structure, even when activated.[8] The energy diagram for the keto−enol acetone radical cation tautomerization is given in Figure 1. Because of the relatively weak C−C bond in ionized acetone (19 kcal/mol,[9] compared to 87 kcal/mol[9] for the neutral), even high energy acetone ions do not isomerize; rather they dissociate to $\mathrm{CH_3{-}C{=}O^+ + CH_3^\bullet}$.

Recently, some elegant experimental[10] and theoretical studies[11] have reported a mechanism by which a gaseous conventional radical cation $[\mathrm{H{-}X{-}Y}]^{\bullet+}$ (e.g., $\mathrm{X = CH_2}$, $\mathrm{Y = OH}$) may rearrange to a more stable distonic isomer $[\mathrm{X{-}Y{-}H}]^{\bullet+}$ via a two-step proton-transfer through interaction with an appropriate base B, according to

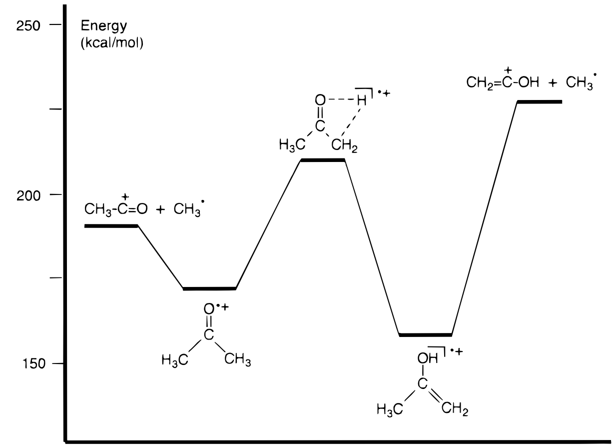

Figure 1. Energy diagram for the acetone keto and enol radical cations. Experimental data taken from refs 5, 7, and 9.

$$[\mathrm{H{-}X{-}Y}]^{\bullet+} + \mathrm{B} \rightarrow \mathrm{B}\cdots\mathrm{H}^+\cdots[\mathrm{X{-}Y}]^\bullet \rightarrow \mathrm{B}\cdots\mathrm{H}^+\cdots[\mathrm{Y{-}X}]^\bullet \rightarrow \mathrm{B} + [\mathrm{X{-}Y{-}H}]^{\bullet+} \quad (1)$$

This process has been termed “proton-transport catalysis”.[10a] It appears that it not only occurs under certain conditions in bimolecular reactions (see below), but that it also is a key step in the dissociation of a variety of oxygen-containing radical cations.[12] Gauld and Radom have evaluated conditions for efficient proton-transport catalysis.[11b] From thermochemical considerations they conclude that efficient catalysis will take place, see eq 1, when the proton affinity (PA) of the base B lies between the PA of [X−Y] at X and at Y. If the PA [B] is significantly lower than the PA [XY] at Y, the first step in eq 1 will not take place. If, on the other hand, PA [B] is significantly larger than PA [XY] at X, then the intermediate complex $\mathrm{B}\cdots\mathrm{H}^+\cdots[\mathrm{X{-}Y}]^\bullet$ will dissociate to $[\mathrm{X{-}Y}]^\bullet$ and $\mathrm{HB^+}$ via a unidirectional proton-transfer. In effect, if PA [B] is intermediate, the barrier becomes negative relative to the separated reactants and products and the base successfully catalyzes the isomerization.[11b] In this paper evidence is presented that such a proton-transport catalysis can also accommodate keto-to-enol ionic tautomerizations. Applying the above arguments to the model keto compound ionized acetone, efficient enolization can take place when a base is chosen such that its PA lies between the PA of the radical $\mathrm{^\bullet CH_2C({=}O)CH_3}$ at C and at O. From ΔH_f $[\mathrm{^\bullet CH_2C({=}O)CH_3}] = -12 \pm 1.5$ kcal/mol[13] and the heats of formation of ionized acetone (172 kcal/mol[9]), its enol (158 kcal/mol[9]), and $\mathrm{H^+}$ (366 kcal/mol[9]), PA [B] should lie between 182 and 196 kcal/mol. Interestingly then, acetone itself, having PA = 197 kcal/mol,[14] would be a suitable candidate.

Acetone was introduced into the chemical ionization source of the McMaster VG ZAB−R mass spectrometer[14] to a maximum indicated pressure of 5×10^{-5} Torr. Unfortunately, under these conditions the acetone radical cations readily and preferentially undergo proton-transfer to acetone (self-protonation) to produce $\mathrm{CH_3C^+(OH)CH_3}$ ($\Delta H_f = 117$ kcal/mol[9]) and $\mathrm{^\bullet CH_2C({=}O)CH_3}$ (ratio m/z 58:m/z 59 = 0.28), a reaction which is exothermic by 15 kcal/mol (ΔH_f [acetone] = − 52 kcal/mol[9]). In addition, an intense signal was found for the proton-bound dimer, but only a small signal was observed for the dimer radical cation (ratio m/z

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116:*m*/*z* 117 = 0.07) which would serve as precursor for the enol of acetone, see eq 1. Nevertheless, the collision-induced dissociation (CID)[14] mass spectrum of the remaining *m*/*z* 58 ions revealed that some, but not complete, enolization had taken effect.

We decided to search for a better base, i.e., one that does not undergo self-protonation and which has the right PA. In addition, the ionization energy (IE) of the base should not be much lower than that for acetone, otherwise ionized acetone will be neutralized by charge exchange. It appeared that benzonitrile might be a more successful candidate, that is, it has the right PA (196 kcal/mol[9]), self-protonation of benzonitrile is now calculated to be endothermic by 7 kcal/mol,[15] and the IE of benzonitrile (9.62 eV[9]) is not much lower than that of acetone (9.71 eV[9]). (Note also that protonation of acetone by ionized benzonitrile is endothermic (by 6 kcal/mol)). Indeed, when C_6H_5CN is introduced into the chemical ionization source (via a quartz probe at room temperature) to a maximum indicated pressure of 1×10^{-4} Torr, the ratio *m*/*z* 103:*m*/*z* 104 was 0.23, showing that only 15% self-protonation takes effect. Other peaks observed in the mass spectrum correspond to dissociation products of ionized benzonitrile itself (*m*/*z* 39, *m*/*z* 63, and *m*/*z* 76), to adducts of these ionic products and benzonitrile (*m*/*z* 142, *m*/*z* 166, and *m*/*z* 179), and to the proton bound dimer (*m*/*z* 207); also, a relatively intense peak is observed for the dimer radical cation at *m*/*z* 206. Peaks in the region 54−61 were absent. Next, a small amount of acetone was injected into the ion source, and a significant peak at *m*/*z* 58 appeared together with a small peak at *m*/*z* 59 (*m*/*z* 58:*m*/*z* 59 = 3). Other peaks appear at *m*/*z* 146 (a complex of C_6H_5CN and $CH_3{-}C{=}O^+$), at *m*/*z* 162 (the proton-bound dimer of benzonitrile and acetone), and at *m*/*z* 204 (a complex of C_6H_5-CN, acetone, and $CH_3{-}C{=}O^+$). Most importantly, and in sharp contrast to the chemical ionization experiments using acetone only, a relatively intense peak for the [“acetone”$\cdots C_6H_5CN]^{\bullet+}$ dimer radical cation was now clearly present at *m*/*z* 161. The CID mass spectrum of the *m*/*z* 58 ions generated in the ion source is shown as item c in Figure 2. The CID mass spectra of the acetone keto and enol ions are well-known;[8] our (partial) reference spectra are shown in Figure 2a and b respectively, and they are characteristically different, especially in the region *m*/*z* 24−*m*/*z* 31.[8] These spectra leave no doubt that the original acetone keto ion has been converted, and virtually completely so, to its enol counterpart.

The CID mass spectra of the [“acetone”$\cdots C_6H_5CN]^{\bullet+}$ complex at *m*/*z* 161 contains two intense peaks of almost equal intensity at *m*/*z* 58 and *m*/*z* 104 (protonated benzonitrile). The CID mass spectrum of these *m*/*z* 58 ions, as recorded in an MS/MS/MS experiment[16] and shown in Figure 2d, reveal that they have the enol structure.[17] This experiment clearly shows that the initially formed [acetone$^{\bullet+}\cdots C_6H_5CN$] adduct has rapidly converted into a [enol acetone$^{\bullet+}\cdots C_6H_5CN$] complex, probably the hydrogen-bridged[18] structure $[CH_2{=}C(CH_3){-}O\cdots H\cdots NC{-}C_6H_5]^{\bullet+}$. *This constitutes definitive evidence that benzonitrile catalyses the enolization.*

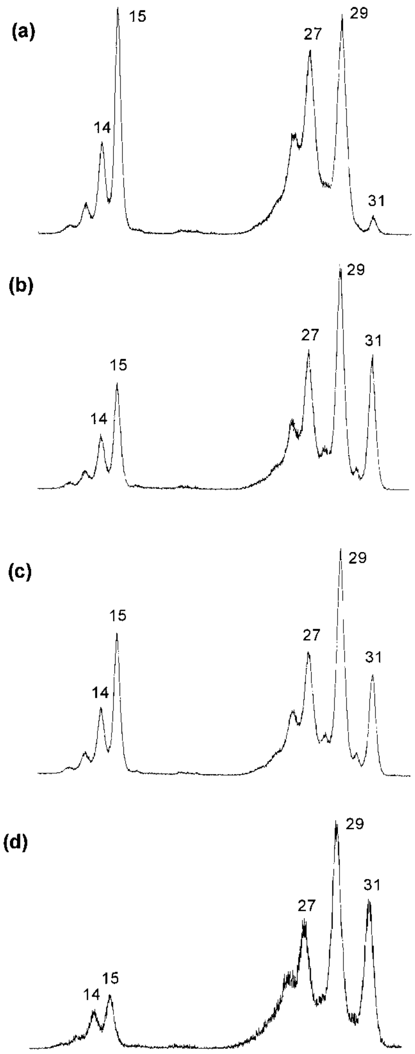

Figure 2. Collision-induced dissociation mass spectra of (a) acetone, reference; (b) enol of acetone, reference; (c) *m*/*z* 58 in the benzonitrile chemical ionization mass spectrum of acetone; (d) the collisionally formed *m*/*z* 58 from the [“acetone”$^{\bullet+}\cdots$benzonitrile] adduct.

Finally we note that if the PA of the base is significantly out of range, enolization does not take effect, as predicted by Gauld and Radom.[11b] For example, for the acetaldehyde$^{\bullet+}$/vinyl alcohol$^{\bullet+}$ tautomerization, the PA of the base should lie between 170 and 185 kcal/mol[19] (or 174 and 189 kcal/mol[20]); as predicted, interaction of ionized acetaldehyde with benzonitrile (PA = 196 kcal/mol) leads to protonated benzonitrile only, and the small amount of remaining *m*/*z* 44 ions have retained the acetaldehyde structure. This paper is dedicated to Professor M. T. Bowers on the occasion of his upcoming 60th birthday and in recognition of his outstanding contributions to gas-phase ion chemistry.

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[15] From $\Delta H_f\ [C_6H_5CN]^{\bullet+} = 274$ kcal/mol,[9] $\Delta H_f\ [C_6H_5CN] = 52$ kcal/mol,[9] $\Delta H_f\ [C_6H_5CNH]^+ = 222$ kcal/mol,[9] and $\Delta H_f\ [C_6H_4CN]^{\bullet} = 111$ kcal/mol; the latter value was obtained using the benzene C−H bond dissociation energy of 111 kcal/mol[9] and $\Delta H_f\ [H]^{\bullet} = 52$ kcal/mol.[9]

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[19] From $\Delta H_f\ [CH_3C(H){=}O]^{\bullet+} = 196$ kcal/mol,[9] $\Delta H_f\ [CH_2{=}C(H)OH]^{\bullet+} = 181$ kcal/mol[9] and $\Delta H_f\ [{}^{\bullet}CH_2C(H){=}O] = 0.2$ kcal/mol.[13]

[20] Using $\Delta H_f\ [{}^{\bullet}CH_2{-}C(H){=}O] = 4.0$ kcal/mol from Mayer, P. M.; Glukhovtsev, M. N.; Gauld, J. W.; Radom, L. *J. Am. Chem. Soc.* **1997**, *119*, 9, 12889.