β to palladium to the carbon α to palladium. An intermediate lacking a β hydrogen, formed from **1** and isobutylene with $R = R' = CH_3$ and $R'' = H$,[24] decomposes by a different pathway to yield an allyl complex with no evidence for the expected olefin oxidation products, isobutyraldehyde or 2-butanone.

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Supplementary Material Available: Experimental details for syntheses and reactions (5 pages). Ordering information is given on any current masthead page.

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[24] ^{1}H NMR (CDCl$_3$) δ 3.32 (2 H, s), 1.74 (6 H, s); NMR yield ~60% based on Pd; IR (CDCl$_3$) $\nu_{N=O}$ 1620 cm^{-1}.

Thermochemistry and Unimolecular Reactions of Ionized 1,2-Dimesityl-2-phenylethanone and 2,2-Dimesityl-1-phenylethanone and Their Enols and Enol Acetates in the Gas Phase

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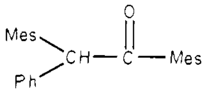
Keto–enol tautomerism of gas-phase ions is a subject of intense current research activity.[1] In all of the reports published to date, one of the tautomers, usually the enol, was produced as a fragment ion by dissociative ionization rather than as a parent ion by direct ionization. The most common route to enol production in the gas phase has been the McLafferty rearrangement reaction. Following Fuson[2a,b] we synthesized the isomeric ketones 1,2-dimesityl-2-phenylethanone (**1**) and 2,2-dimesityl-1-phenylethanone (**2**) and their stable isomeric enols *Z*-**3** and **4** as well as the *E*- and *Z*-enol acetates **5** and **6**[2a] and the enol acetate **7**[2b] and determined their geometric structures.[2c,d] For the first time this enables (i) ionization of both enol and keto forms directly in the gas phase, thus obtaining the relative heats of formation of the ions, and observation of their unimolecular reactions; (ii) comparison of the behavior of the ionized enols formed by cleavage of the acetate esters, with that of the directly ionized enol and ketone forms.

Table I. Equilibrium Data, Ionization Potentials, and $T_{1/2}$ Values for the Reactions of **1**–**7**

compd	IP, eV	$T_{1/2}$, meV (transition)	$\Delta G°$, kcal mol^{-1} (process)
1	8.1 ± 0.2	12.6 ($356 \rightarrow 147$)	0.6,^{a} 1.12^b ($1 \rightleftharpoons 3$)
3	7.5 ± 0.2	34.5 ($356 \rightarrow 147$)	0.57^a ($1 \rightleftharpoons 3$) 1.06^b
2	7.6 ± 0.1	20.6 ($356 \rightarrow 105$)	−0.5 ± 0.1^a ($2 \rightleftharpoons 4$)
		24.7 ($356 \rightarrow 251$)	−1.12^b
4	7.5 ± 0.1	33.3 ± 3 ($356 \rightarrow 105$)	−0.51 ± 0.13^a ($2 \rightleftharpoons 4$)
		37.3 ($356 \rightarrow 251$)	−0.93^b
5		33.4 ± 2.0 ($356 \rightarrow 147$)	
6		35.3 ± 0.1 ($356 \rightarrow 147$)	
7		33 ± 3 ($356 \rightarrow 105$)	
		37.0 ($356 \rightarrow 251$)	

^{a} In hexane at 335 K. ^{b} In PhCl at 405 K.



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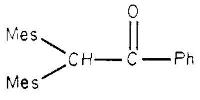

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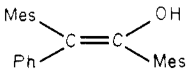

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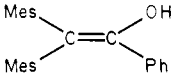

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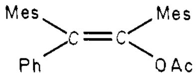

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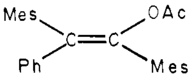

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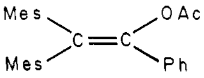

7

Mes = 2,4,6-$Me_3C_6H_2$

Metastable ion dissociations were studied on a Varian MAT 311 instrument (reverse Nier–Johnson geometry) by scanning the accelerating voltage. Scans were carried out automatically and accumulated with the aid of a D116 Digital Computer Controls minicomputer. Ionization potentials were determined by the semilogarithmic method[3] using benzene (IP = 9.5 eV) and argon (IP = 15.8 eV) as reference standards, on a Varian MAT 711. The results are given in Table I.

In order to evaluate the contribution of the neutral species to the ΔH_f difference of the ions, the two ketone–enol pairs were equilibrated in hexane and chlorobenzene in the presence of CF_3COOH. **1** is less stable than **3** by 0.6–1.1 kcal mol^{-1}, whereas **2** is more stable than **4** by 0.5–1.0 kcal mol^{-1} (Table I).[4]

The ionization potential of the ketone **1** is 0.6 eV (13.8 kcal mol^{-1}) higher than for the enol **3**. The enol ion is thus more stable than the keto ion by 14.4–14.9 kcal mol^{-1}. This is in line with data for other enol and ketone ions, where the enol ion is more stable by 14–31 kcal mol^{-1}.[5] Surprisingly, the IP values are almost identical for the ketone **2** and the enol **4**. This is not easily explained by the structural change and may reflect ionization of **2** at the dimesitylmethyl moiety rather than at the C=O group.

Kinetic-energy release determinations were used to probe for differences between the ketone and enol ions. Enol ions were obtained by direct ionization of **3** and **4** as well as by a four-center

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Table II. MIKE Spectra of m/e 356 and (O-Deuterated) m/e 357 Ions[a]

	compd							
m/e	1	3	5	6	2	4	7	4-OD
341 (342[b])	23.9	24.7	24.5	23.4	(100.0)	(100.0)	(100.0)	(100.0)
338	16.8	22.0	22.0	25.0				
265 (266[b])	(100.0)	(100.0)	(100.0)	(100.0)	1.7	0.8	0.7	9.8
251 (252[b])					7.2	7.3	6.1	6.8
236 (237[b])	44.0	37.0	37.2	35.1	3.6	3.1	2.7	6.0
147	13.4	10.5	10.1	9.4				
105					0.4	0.5	0.3	0.5

[a] Low abundance ions have not been included. [b] These m/e values relate to O-deuterated **4** only.

rearrangement of ionized **5**–**7**.[6] The overall 356^+ MIKE spectra of **1**, **3**, **5**, and **6** or **2**, **4**, and **7** are very similar (Table II). The four compounds **1**, **3**, **5**, and **6** showed the metastable transition $356^+ \rightarrow 147^+$. The ion at m/e 147 is $C_{10}H_{11}O^+$ according to high-resolution mass spectrometry and is presumably the mesitoyl ion $2,4,6\text{-}Me_3C_6H_2C{\equiv}O^+$. Compounds **2**, **4**, and **7** showed the two metastable transitions $356^+ \rightarrow 105^+$ ($PhCO^+$), $356^+ \rightarrow 251^+$ (Mes_2CH^+, by high resolution). A study of O-deuterated **4**, ($Mes_2C{=}C(OD)Ph$, m/e 357) showed a major m/e 252 peak, corresponding to the Mes_2CD^+ ion (Table II). Kinetic-energy release values ($T_{1/2}$) were calculated from the metastable peak widths at half-height. The peak shapes for the $356^+ \rightarrow 147^+$ reaction of **3**, **5**, and **6** were identical within the experimental error: the exponent for a Gaussian-type peak[7] (n) equals 1.8. In contrast, the $T_{1/2}$ value for **1** is definitely lower, and the peak shape is different, $n \simeq 1.4$. Likewise, the $T_{1/2}$ values for **4** and **7** for both the $356^+ \rightarrow 105^+$ and the $356^+ \rightarrow 251^+$ reactions are identical[8] but those for **2** are lower (Table I).

Appearance energies (AE) were determined in order to evaluate the activation energy difference (ΔE_a) between the enol and ketone dissociations. The values have been measured for the metastable ion transition $356^+ \rightarrow 147^+$ in **1** and **3**, using the metastable transition $398^+ \rightarrow 147^+$ for $Mes_2C{=}C(OH)Mes$ as the reference reaction in both cases. The value for **3** is 2.1 eV higher than for **1**, indicating a ΔE_a value of 2.7 eV.

Two important conclusions emerge from the data: (a) The same enol ions are formed from the enol and the enol acetates, i.e., 3^+ from **3** and **6**, and 4^+ from **4** and **7**. This is additional direct evidence that the loss of the CH_2CO fragment from an enol acetate gives the enol in a four-center transition state. Previous evidence[6] was based on the difference between the relative abundances of several peaks which are presumably derived from the peak at m/e of the ionized ketone in the mass spectra of the ketone and the enol acetate. Here we show that the $T_{1/2}$ values are similar, starting from the stable enols and their acetates. Since **5** should give the unknown E isomer of the enol **3** by a four-center fragmentation, the identy of $T_{1/2}$ values suggests either that $E \rightleftharpoons Z$ interconversion of the enols is rapid or that the geometry of the enol has little influence on its cleavage to the mesitoyl ion. (b) The enol ions are not freely interconverting to the keto forms below their respective dissociation limits, since in this case the kinetics-energy releases and metastable peak shapes should have been the same. The data suggest that the ionized enol 3^+ undergoes a rate-determining isomerization in which the intermediate ionized ketone 1^+ is formed with ≥2 eV energy above the dissociation limit. Consequently, the $T_{1/2}$ value for the enol dissociation is higher than for the keto dissociation.

Further studies on this and related systems which should throw light on the mechanistic question as to whether the enols dissociate to form the aroyl cation via a rate-determining isomerization to the keto form are in progress.

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[8] Due to the lower intensity of the metastable peak for the 356 → 105 reaction, the $T_{1/2}$ values are less accurate than for the 356 → 251 reaction.

Proton-Coupled Electron Transfer between $[Ru(bpy)_2(py)OH_2]^{2+}$ and $[Ru(bpy)_2(py)O]^{2+}$. A Solvent Isotope Effect (k_{H_2O}/k_{D_2O}) of 16.1

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We reported recently that oxidation of the complex $[Ru(bpy)_2(py)OH_2]^{2+}$ occurs in two reversible, one-electron steps (Scheme I).[1] The redox chemistry of the system is remarkable in that the Ru(IV)/Ru(II) couple appears to undergo mechanistically well-defined multiple electron-transfer pathways via net O-atom or hydride ion transfers.[2,3] In addition, the Ru(IV)/Ru(II) couple of the related complex $[Ru(trpy)(bpy)OH_2]^{2+}$ has been shown to provide the basis for the electrocatalytic oxidation of a series of oragnic substrates including aromatic hydrocarbons, olefins, and primary and secondary alcohols.[4]

The one-electron-transfer redox chemistry of these systems is also of potential interest, arising from the proton demands imposed by simple electron transfer. Oxidation of $[Ru(bpy)_2(py)OH_2]^{2+}$ above pH ~2 results in $[Ru(bpy)_2(py)OH]^{2+}$. Further oxidation by one electron gives the oxo complex, $[Ru(bpy)_2(py)O]^{2+}$, for which there is no evidence for protonation of the oxo ligand, even in strongly acidic media.

The importance of a proton demand upon electron transfer is readily apparent in the comproportionation reaction between the Ru(IV) and Ru(II) complexes in eq 1, which is favored in the

$$[Ru(bpy)_2(py)H_2O]^{2+} + [Ru(bpy)_2(py)O]^{2+} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} 2[Ru(bpy)_2(py)OH]^{2+} \quad (1)$$

forward direction by a driving force $\Delta G°$ of −2.5 kcal mol^{-1} ($K_{com} = k_f/k_r = 72$, $\Delta E° = 0.110$ V) at 25 °C for $2 < pH < 9$. Stopped-flow kinetics studies show that this reaction is first order in both Ru(II) and Ru(IV). The reaction is remarkable both for the absence of a pH dependence over a broad pH range (2.4–9.2) and slowness of the electron-transfer rate constant ($k_f = k_{H_2O} = (2.10 \pm 0.02)10^5$ M^{-1} s^{-1} at 25.3 °C, $I = 0.10$ M, Na_2SO_4) when

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