223. Ionization Energies of 1-R-2,2-dimesitylethenols, 1,2-Dimesityl-2-phenylethenol, and Some of their Keto Tautomers

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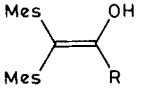
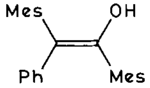
The He(Iα) PE spectra of the two pairs of **1**(Ph)-**3** and **2**–**4** have been recorded and assigned by comparison with spectra of related molecules, or by using simple MO arguments. This analysis shows that the PE spectra are in agreement with the assumption that the twist angles observed in the crystalline state are more or less conserved in the gas phase. The observed first adiabatic ionization energies I_1^a allow the calculation of the molar reaction enthalpy $\Delta_r H_m^\ominus$ which accompanies the enolization of the radical cations of the title compounds. It is found that $\Delta_r H_m^\ominus \approx -70$ kJ mol^{-1} is roughly the same for both keto/enol pairs, in qualitative and quantitative agreement with expectation. These results complement and correct ionization energies determined previously by mass spectrometric methods and conclusions based on them.

Introduction. – The first ionization energies of the title molecules (**1**(Ph), **2**, **3**, **4**, in that order) have been determined previously [1] on a *Varian-MAT-711* mass spectrometer, using the method described in [2]. From these data, reaction enthalpies $\Delta_r H_m^\ominus$ for the change ketone radical cation→enol radical cation, *i.e.* $\mathbf{3}^+ \rightarrow \mathbf{1}(\mathrm{Ph})^+$ and $\mathbf{4}^+ \rightarrow \mathbf{2}^+$, were derived on the basis of the $\Delta_r H_m^\ominus$ values of the corresponding neutral parent pairs. A feature which was difficult to explain was the similarity in the apparent ionization potentials for **1**(Ph) and **3**, whereas those for **2** and **4** were different. In view of this, it seemed of interest to reinvestigate the problem using PE spectroscopy.



R = H
= Me
= Ph

1(R)



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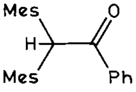

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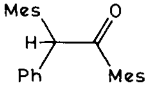
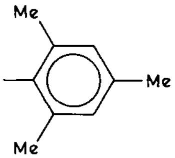


4

Mes =



Experimental. – The enol **1**(H) was prepared according to *Biali* and *Rappoport* [3] by a modification of the method of *Fuson* and *Rowland* [4]. Enols **1**(Me) [5] **1**(Ph) [5], and **2** [6], and ketones **3** [5] and **4** [6] were prepared according to *Fuson et al.*

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The ionization energies I_j^m, *i.e.* the positions of the band maxima in the He(Iα) PE spectra of the six molecules **1**(R) to **4** are collected in the *Table*. Sample spectra, *e.g.* of **1**(H), **1**(Ph), and **3** are shown in the *Figure*. Because of the low volatility of the compounds, the PE spectra had to be recorded at temp. in the range 100° to 150°, depending on the size of the molecules. The lack of fine structure of the PE features is presumably due to the excitation of low-frequency vibrations in the radical-cation states and to the finite conformational changes in the parent molecules within the range imposed by steric interference between the bulky Ph and Mes groups. In addition, the broad features, such as ② in the PE spectrum of **1**(H), ② and ③ in that of **1**(Ph), or ① and ② of **3**, are due to the superposition of individual bands which can not be deconvoluted. As a consequence, the positions I_j^m of the band system maxima can, at best, be estimated to ±0.05 eV or even ±0.1 eV, and their values are not necessarily close to the vertical ionization energies I_j^v of their components.

Table. *Ionization Energies*. The values I_j^m refer to the positions of the band maxima, the I_1^a to the (adiabatic) onset of band ①. Estimated errors: ±0.05 eV, if second decimal given as subscript, otherwise ±0.1 eV.

	①		②	③	④
	I_1^m/eV	I_1^a/eV	I_2^m/eV	I_3^m/eV	I_4^m/eV
1(H)	7.6_0		8.4_5	9.1_5	11.2[a])
1(Me)	7.5_0		8.4_5	(9.1)[b])	11
1(Ph)	7.2_5	6.9_0	8.3_5	8.9(9.3)[c])	11.3[d])
2	7.4_0	7.1_5	8.4_5	9.2	
3	8.3_0	7.7	9.2_0	11	
4	8.5[e])	7.8	9.0[e]) (9.5)[c])	11	

[a]) Preceeded by a shoulder at ~ 10.7 eV.

[b]) Shoulder, strongly overlapped by the band system ②.

[c]) Shoulder.

[d]) This maximum is preceeded by a shoulder at ~ 10.6 eV; unidentified.

[e]) Band systems ① and ② form an almost continuous feature which can not be properly deconvoluted. The maximum ① is only slightly more prominent than ②.

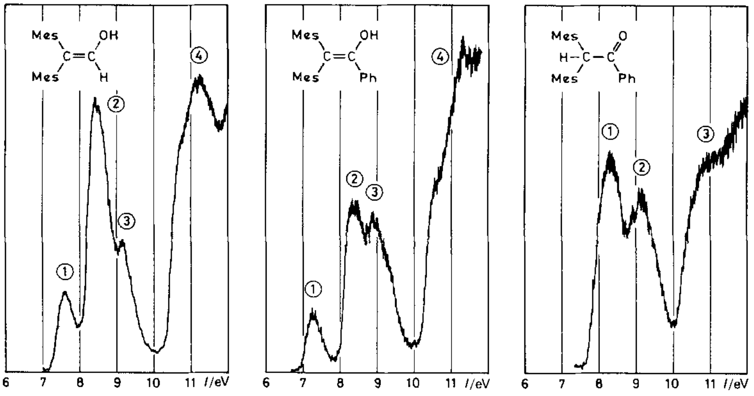

Fig. *He(Iα) PE spectra of* **1**(H), **1**(Ph), *and* **3**

The effects quoted above are also responsible for the difficulty experienced when trying to assess the adiabatic ionization energies I_1^a of bands ①, *e.g.* in the PE spectra of **1**(Ph), **2**, **3**, and **4**. In the absence of other ancillary evidence, we have assumed that I_1^a corresponds to the band onset of ①, *i.e.* to the ionization energy where the signal begins to exceed significantly the recording noise level. Thus, the I_1^a values quoted in the *Table* are good only to ±0.1 eV.

The mass-spectrometrically determined ionization energies *I*(MS) given in [1] compare as follows with the present I_1^m values. For the enols **1**(Ph) and **2**, the agreement between the two sets of data is reasonable: **1**(Ph),

I(MS) = 7.5 ± 0.1 eV, $I_1^m = 7.2_5$ eV; **2**, I(MS) = 7.5 ± 0.2 eV, $I_1^m = 7{,}4_0$ eV. On the other hand, the values for **3** differ considerably, *i.e.* I(MS) = 7.6 ± 0.1 eV, $I_1^m = 8.3_0$ eV and, to a minor extent those of **4**, *i.e.* I(MS) = 8.1 ± 0.2 eV, I_1^m = 8.5 eV. Note that the I(MS) values refer to I(MS) = 9.5 eV for benzene as a standard, whereas the PE data correspond to $I_1^m = I_1^v = 9.25$ eV for benzene. Finally, it should be mentioned that the adiabatic ionization energies I_1^a of **1**(Ph) and **2** are 0.3_5 and 0.2_5 eV lower than I_1^m, those of **3** and **4** lower by 0.6 and 0.7 eV, respectively. A more detailed comparison of the PE and MS data indicates that the latter are affected by systematic and stochastic errors in excess of the 'error limits' quoted, which refer to the reproducibility of the data with a given experimental set-up and a particular evaluation method.

Assignment. – Although the gross features of the PE spectra of **1**(R)–**4** can be assigned without difficulty, a more detailed discussion, *e.g.* one of conformational relevance, is not possible because of the already mentioned overlap of the bands and the presumed presence of a mixture of conformers at the recording temperature. Indeed, it is known from dynamic NMR data that, at room temperature, there is a rapid racemization of the enantiomeric 'propellers', *i.e.* a sign reversal of the twist angles between the vinyl and Mes groups [7].

The PE spectrum of vinyl alcohol ($CH_2 = CHOH$), prepared by thermolysis of cyclobutanone, has been recorded and interpreted by *Albrecht et al.* [8]. Its low-ionization energy part consists of a π^{-1} band ① at $I_1^v = 9.52$ eV ($^2A''(\pi)$), $I_1^a = 9.18$ eV, and a band system ② in the range 13.6 eV to 14.1 eV, assigned to two σ^{-1} and a π^{-1} band. The latter band system could not be deconvoluted. If π stands for the double-bond two-centre π-orbital and 2p(O) for the oxygen 2p orbital in phase with π, then band ① is associated with the HOMO of type $\pi - 2p(O)$ and the other π^{-1} band imbedded in ② with an orbital of type $\pi + 2p(O)$, disregarding normalization and relative weight factors.

Accordingly, there is no doubt that the bands labeled ①, around 7.3 to 7.5 eV in the PE spectra of **1**(R) (R = H, Me, Ph) and **3** are due to electron ejection from a $\pi - 2p(O)$-type HOMO shifted by about 2 eV towards lower ionization energies, because of conjugative interaction with the mesityl- and Ph-group π orbitals and with ribbon [9] orbitals. These two types of interaction are additive (in a first approximation), their relative size depending on the twist angles θ (*cf.* below).

Assuming for the moment that the twist angles θ between the Mes groups and the double bond in **1**(H) are small enough for the π/π interaction being the dominant factor responsible for the band shift, and designating the degenerate frontier orbitals of mesitylene by φ_S and φ_A (S = symmetric, A = antisymmetric with respect to a plane through C(2) and C(5) and perpendicular to the molecular plane), then the PE spectrum of **1**(H) can be qualitatively assigned as follows:

Band	I^m/eV	Orbital type	
①	7.6_0	$(\pi-(\varphi_{S,a}+\varphi_{S,b}))-2p(O)$	
②	8.5	$\varphi_{A,a}$; $\varphi_{A,b}$; $(\varphi_{S,a}-\varphi_{S,b})$	(1)
③	9.1_5	$(\pi+(\varphi_{S,a}-\varphi_{S,b}))-2p(O)$	

The indices 'a' and 'b' refer to one or the other of the two Mes groups. Note again that the orbital-type designation neglects the normalizing factor, the relative weight of the basis functions in the linear combination, and the contribution of lower-lying basis orbitals.

From crystallographic data, it is known that the twist angles θ cover a range of about 45° to 55° [10]. Thus, in dimesityl ketene ($Mes_2C{=}C{=}O$) the twist angles are θ = 57° and θ = 48° (in spite of molecular symmetry) [10]. For **2**, one observes $\theta(\beta{-}Ph)$ = 38° and θ $(\beta{-}Mes)$ = 74°, a significant difference corroborated by molecular mechanics calculations [11]. Finally, the twist angles in **1**(H) are $\theta = 57°$ for Mes *cis* to OH and $\theta = 50°$ for Mes *trans* to OH, according to the crystallographic data [12]. It follows that the π/ribbon orbital interaction may well be as important as the π/π interaction.

It is easy to show that assignment (*1*) is also quantitatively rather reasonable, even if we relax the unrealistic assumption that π/π interaction dominates. *Kobayashi et al.* have recorded the PE spectra of Me substituted styrenes [13] (see also [14]), in particular that of 2,4,6-trimethylstyrene. In the PE spectrum of the latter molecule, the first three bands at $I_j^m = 8.33$, 8.65, and 9.83 eV have been assigned to orbitals of type $\varphi_S - \pi$, φ_A, and $\varphi_S + \pi$, respectively. If this assignment is interpreted in terms of a naive orbital treatment using only the three basis orbitals φ_S, φ_A, and π, one finds that the basis energies are $A(\varphi_S) = A(\varphi_A) = -8.6_5$ eV, $A(\pi) = -9.5_0$ eV, and $B_{\varphi\pi} = \langle\varphi_S|\mathrm{H}|\pi\rangle = -0.6_0$ eV. Note that $A(\varphi_S) = A(\varphi_A)$ are practically identical to $A(e'') = -8.40$ eV of mesitylene [15] [16] and $A(\pi)$ almost the same as for alkyl-substituted ethenes $CH_2{=}CHR$, [15] [17], *e.g.* $A(\pi) = -9.7_5$ to -9.4_5 eV for R = Me to *t*-Bu.

One of the important results reported in [13] concerns the experimental and theoretical assessment of the angular dependence, *i.e.* the dependence on the twist angle θ of the conjugation between the benzene and double-bond moieties in Me-substituted styrenes (*cf.* also [14]). For styrene itself, where $\theta = 0°$, the cross-term $B^{\circ}_{\pi\varphi} = \langle\pi|\hat{\mathrm{H}}|\varphi_S\rangle$ has the value $B^{\circ}_{\pi\varphi} = -1.0_0$ eV which corresponds to a standard β value between two carbon 2p AOs, separated by a non-essential double bond, of $\beta = -2.4_5$ eV. This is exactly the same value as that derived from conjugated polyenes [18]. Increasing the twist angle θ leads first to a reduction of the cross-term according to $B_{\pi\varphi}(\theta) \approx B^{\circ}_{\pi\varphi}\cos\theta$, as long as the break-down of σ/π separation does not become too severe. For larger angles of θ, hyperconjugation of the double-bond π orbital with the benzene $\sigma\,(e_{2g})$ ribbon orbitals becomes more and more important, so that for $\theta = 90°$ one observes still significant shifts relative to the basis orbital energies. This is fully supported by semi-empirical calculations reported in [13].

For this reason, one should be careful to translate the cross-term $B_{\pi\varphi} = -0.6$ eV reported for 2,4,6-trimethylstyrene into a twist angle θ, although the simple-minded result obtained according to $\theta = \arccos\,(B_{\pi\varphi}/B^{\circ}_{\pi\varphi}) = \arccos 0.6 = 53°$ seems rather reasonable. In fact, this value fits rather nicely the twist angles derived by *Suzuki*, $\theta = 49°$ [19] and by *Braude* and *Sondheimer*, $\theta = 54°$ [20] from UV data.

The above information can now be used to rationalize the PE spectra of **1**(R) and **2** within a *Hückel*-type formalism. The following parameters suggest themselves for **1**(H):$A(\varphi_S) = A(\varphi_A) = -8.4$ eV and $B_{\pi\varphi} = -0.6$ eV, as shown in the previous paragraph, $A(2p(O)) = -12.6$ eV and $B_{\pi 2p(O)} = -1.7$ eV from [8], and $A(\pi) = -8.5$ eV, taking into account the presence of two Mes groups. Although such a model calculation does certainly not qualify as a theoretical treatment, the result obtained in this fashion is surprisingly good, and completely confirms the assignment (*1*) of the PE spectrum of **1**(H):

Band	ε_j/eV		Orbital	
	exp.	calc.		
①	-7.6_0	-7.3	$0.77\pi - 0.42(\varphi_{S,a} + \varphi_{S,b}) - 0.25\ 2p(O)$	
②	-8.5	-8.4	$\varphi_{A,a};\ \varphi_{A,b};\ (\varphi_{S,a} - \varphi_{S,b})/\sqrt{2}$	
③	-9.1_5	-9.0	$0.54\pi + 0.57(\varphi_{S,a} + \varphi_{S,b}) - 0.25\ 2p(O)$	(2)
		-13.2	$0.35\pi + 0.04(\varphi_{S,a} + \varphi_{S,b}) + 0.94\ 2p(O)$	

Replacement of H by Me or Ph in **1**(H), to yield **1**(Me) and **1**(Ph), leads to an upward shift of the orbital energy ε_1 by 0.1 or 0.3_5 eV, respectively, which is roughly half of what one would expect on the basis of a first-order-perturbation calculation, assuming that the introduction of these substituents in a geminal position to the OH group leaves the conformations of the Mes moieties in **1**(Me) and **1**(Ph) unchanged with respect to **1**(H). This assumption is supported by the solid state [10] and solution [3] data. On the other hand, switching the Ph and a Mes group of **1**(Ph) to yield **2**, leads to a lowering of ε_1 which can be explained as being due to an increase of one of the twist angles θ in the latter molecule, as suggested by the crystallographic results [10] and the molecular-mechanics calculations [11].

The assignment of the PE spectra of the ketones **3** and **4** is a simple matter, because of the known assignments of the PE spectra of benzyl methyl ketone [21] and of 1,1-diphenylacetone [22]. For the latter molecule, the four π^{-1} bands are found at $I_j^m = 8.60$, 9.05, 9.05, and 9.4 eV, forming a single unresolved band system. The oxygen lone-pair band at 9.7 eV can be detected as a shoulder at the high energy end of this system. Accordingly, band ① of **3** and **4** has to be associated with the Mes-group π orbitals and band ② with those of the Ph group. The slight shoulder at around 9.5 eV could be due to electron ejection from the oxygen lone-pair of **3**.

Reaction Enthalpy $\Delta_r H_m^\theta$ for the Ketone→Enol Reaction. – The reaction enthalpies $\Delta_r H_m^\theta = \Delta_f H^\theta$ (Enol) – $\Delta_f H^\theta$ (Ketone) have been determined previously for the pairs **3**, **1**(Ph) [1] [23] and **4**, **2** [1] from equilibration data in hexane and PhCl in the presence of CF_3COOH:

	$\Delta_r H_m^\theta(\Delta_r\varepsilon)$	
4→**2**	–2.5 to –4.6 kJ mol^{-1} (–0.03 to –0.05 eV)	
3→**1**(Ph)	0.0 to +4.2 kJ mol^{-1} (+0.0 to +0.04 eV)	(3)

These data and the ionization energies I_1^m and I_1^a of the pairs **3**, **1**(Ph) and **4**, **2** yield the $\Delta_r H_m^\theta$ values given below, for the ketone→enol reaction of the radical cations, *i.e.* $\mathbf{3}^+\to\mathbf{1}(\mathrm{Ph})^+$ and $\mathbf{4}^+\to\mathbf{2}^+$.

	Adiabatic		Vertical		
	$\frac{-\Delta_r H_m^\theta}{\text{kJ mol}^{-1}}$	$\frac{-\Delta_r\varepsilon}{\text{eV}}$	$\frac{-\Delta_r H_m^\theta}{\text{kJ mol}^{-1}}$	$\frac{-\Delta_r\varepsilon}{\text{eV}}$	(4)
$\mathbf{3}^+\to\mathbf{1}(\mathrm{Ph})^+$	72 ± 15	$0.7_5 \pm 0.1_5$	96 ± 10	$1.0_0 \pm 0.1$	
$\mathbf{4}^+\to\mathbf{2}^+$	67 ± 15	$0.7_0 \pm 0.1_5$	111 ± 10	$1.1_5 \pm 0.1$	

The errors given for the adiabatic case are lower limits, and it could well be that the true errors are even larger, because of the uncertainties attached to I_1^a. The previously reported data [1] are $\Delta_r H_m^\theta(\mathbf{4}^+\to\mathbf{2}^+) = -61$ kJ mol^{-1} in perfect agreement with the present adiabatic value. On the other hand, the former observation that $\Delta_r H_m^\theta(\mathbf{3}^+\to\mathbf{1}(\mathrm{Ph})^+)$ is practically zero could not be confirmed. In fact, the reaction enthalpy is the same as for $\mathbf{4}^+\to\mathbf{2}^+$, well within the limits of error.

It should be noted that the adiabatic $\Delta_r H_m^\theta$ values quoted above in (*4*) are in line with previous observations (*cf.* ref. in [1] [24]) and with theoretical calculations [24]. However, a more detailed comparison is not possible, because of the special features inherent in the large molecules studied in this work.

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