Resonance electron capture by uracil derivatives

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The enol forms of uracil and its derivatives were detected in the gas phase by mass spectrometry. The $[M - H]^-$ ion is produced by resonance electron capture to the lowest unoccupied molecular orbitals, the process being accompanied by the detachment of the hydrogen atom from the nitrogen atom of the diketo form (low-energy peak at 0.8 eV) and from the oxygen atom of the enol form (in the energy region of 1.4 eV). The gas phase contains ~10^{-3}% of the enol form.

Key words: resonance electron capture, negative ion, enol form, uracil.

Interest in the tautomerism of nitrogen bases of nucleic acids is associated with a possible involvement of rare isomer forms in the formation of incorrectly paired bases upon DNA replication.[1,2]

Most studies dealing with uracil and its analogs were carried out in the condensed state. In the gas phase, these compounds have been studied in much less detail. Earlier,[3] fluorescence studies have demonstrated that uracil and its certain derivatives can exist in the enol form to the extent of ~10^{-8}% of the amount of the diketo form at 500 K.

In the present study, we examined the behavior of uracil (**1**) and its derivatives **2—9** under conditions of resonance electron capture.

Experimental

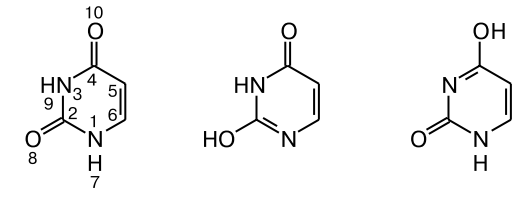
Mass spectra were obtained on an MI-1201 mass spectrometer modified for measuring negative ions.[4] The electron energy scale was calibrated against the maxima of the effective yield curves of the SF_6^- and NH_2^- ions from SF_6 (0 eV) and NH_3 (5.65 eV), respectively. The source pressure was ~10^{-6} Pa. The inlet temperature was carefully controlled.

Commercial compounds **1—4** and **6—9** of high-purity grade (Reakhim, Russia) were used in experiments. 5-Hydroxy-6-methyluracil (**5**) was synthesized according to a known procedure.[5]

Results and Discussion

The mass spectra of the compounds under study (Table 1) show $[M - H]^-$ ions, which are formed at epithermal electron energies (0.8—1.8 eV), and $[NCO]^-$ ions formed in several electron energy regions. The negative molecular ion is observed only for compound **7** containing the NO_2 group, which makes the major contribution to the lowest unoccupied molecular orbital. It is this orbital to which electron capture occurs.

It is known[6—8] that uracil and its analogs can exist both in the diketo form (**A**) and five possible enol forms (**B—F**). In the gas phase, the form **B** is the most stable of all enol forms.



Apparently, the $[M - H]^-$ negative ions are produced from uracil and its derivatives in the low-energy region by electron capture to the lowest unoccupied MO, the process being accompanied by the detachment of the H atom from the NH group, the OH group of the enol form, and, probably, from the unsubstituted CH group. The detachment of the H atom from the nitrogen atom of the diketo

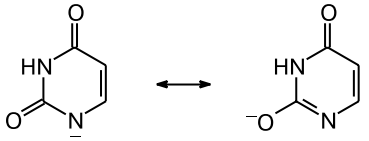


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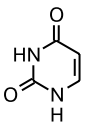
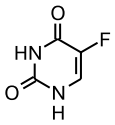
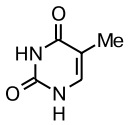
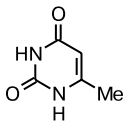
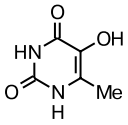
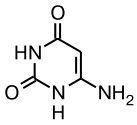
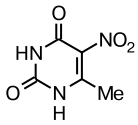
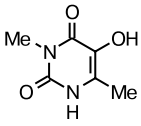
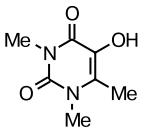
Table 1. Resonance electron capture mass spectra of uracil (**1**) and its derivatives (**2—9**)

Compound		m/z (I_{rel} (%))/E/eV
	(**1**)	111 $[M - H]^-$ (100)/0.8, (79)/1.4; 95 $[M - HO]^-$ (2.1)/3.5; 94 $[M - H_2O]^-$ (13)/3.0; 83 $[M - HCO]^-$ (32)/2.1, (5)/5.9; 42 $[NCO]^-$ (7.8)/1.8, (5.6)/2.3, (3)/4.4, (3.8)/6.0; 26 $[CN]^-$ (20)/1.8, (10)/3.8; 17 $[HO]^-$ (28)/6.5, (18)/8.4
	(**2**)	129 $[M - H]^-$ (100)/0.7, (91)/1.4, (16)/3.6; 86 $[M - NHCOH]^-$ (1.5)/6.1; 59 $[M - CONHCO]^-$ (14)/6.5; 58 $[NHCONH]^-$ (6)/7.1; 42 $[NCO]^-$ (32)/4.4, (27)/6.4
	(**3**)	125 $[M - H]^-$ (100)/1.0, (79)/1.6; 97 $[M - HCO]^-$ (3.5)/5.7, (2.5)/7.8; 71 $[CONHCO]^-$ (1.7)/8.7; 68 $[M - NHCONH]^-$ (0.6)/8.5; 58 $[NHCONH]^-$ (3.6)/4.5, (2)/5.9; 42 $[NCO]^-$ (24)/1.9, (17)/4.1, (30)/6.4, (19)/7.4; 17 $[HO]^-$ (7)/6.6
	(**4**)	125 $[M - H]^-$ (100)/0.9, (27)/1.5; 97 $[M - HCO]^-$ (0.9)/7.7; 84 $[M - NCO]^-$ (1)/5.7; 71 $[CONHCO]^-$ (<0.1)/7.5; 68 $[M - NHCONH]^-$ (0.8)/6.0, (0.7)/8.3; 42 $[NCO]^-$ (3.6)/1.7, (5)/4.3, (11)/6.2
	(**5**)	141 $[M - H]^-$ (100)/1.1, (88)/1.5; 125 $[M - OH]^-$ (2)/1.3; 99 $[M - NCOH]^-$ (1.6)/2.7; 71 $[CONHCO]^-$ (1.2)/7.8; 58 $[NHCONH]^-$ (2.3)/4.4, (20)/5.6; 42 $[NCO]^-$ (18)/5.8, (22)/6.7, (11)/9.4; 26 $[CN]^-$ (2.8)/3.9
	(**6**)	126 $[M - H]^-$ (100)/1.0, (55)/1.6; 111 $[M - NH_2]^-$ (1.6)/1.2; 83 $[M - NHCOH]^-$ (12)/1.8, (6)/5.6; 71 $[CONHCO]^-$ (2.7)/8.2; 58 $[NHCONH]^-$ (5)/5.5; 42 $[NCO]^-$ (35)/1.7, (24)/2.2; 15 $[NH]^-$ (0.9)/6.6
	(**7**)	171 $[M]^-$ (0.5)/0.2; 170 $[M - H]^-$ (0.8)/0.6, (0.7)/0.9; 154 $[M - OH]^-$ (0.6)/3.3; 128 $[M - NHCO]^-$ (2.8)/3.3; 125 $[M - NO_2]^-$ (8.7)/0.5, (1.8)/1.0; 46 $[NO_2]^-$ (3.3)/0.4; 42 $[NCO]^-$ (6)/3.9; 16 $[O]^-$ (100)/4.5, (38)/7.5
	(**8**)	155 $[M - H]^-$ (100)/1.2, (41)/1.5; 141 $[M - Me]^-$ (9)/1.4, (2)/8.0; 127 $[M - HCO]^-$ (0.9)/4.1; 113 $[M - NHCO]^-$ (2.5)/6.3, (1.6)/8.9; 42 $[NCO]^-$ (5)/9.3
	(**9**)	169 $[M - H]^-$ (100)/1.6, (18)/4.5; 155 $[M - Me]^-$ (12)/1.6, (5)/4.2, (11)/9.2; 153 $[M - OH]^-$ (3.3)/9.1; 113 $[M - CONMe]^-$ (1.8)/9.2; 42 $[NCO]^-$ (11)/6.4, (26)/9.7; 26 $[CN]^-$ (1.1)/9.6

form and from the oxygen atom of the enol form gives rise to the following resonance-stabilized structure of the negative ion.

Since the structure of this ion is the same in both cases, the electron affinity of the $[M - H]^{\bullet}$ radical is also the same. In this case, the energy difference of the $[M - H]^-$ ion formation is determined by the difference between the energies of the N—H or O—H bond cleavage, which are ~84 and ~102.3 kcal mol^{-1}, respectively.[9] Therefore, this difference is ~0.8 eV, which is comparable with the difference between two closely spaced low-energy $[M - H]^-$ resonances* (see Table 1).

Presumably, the first and second peaks in the effective yield curve of the $[M - H]^-$ ions (in the energy regions of 0.8 and 1.4 eV, respectively) are associated with the de-

* The true difference between the peaks is, apparently, larger taking into account incomplete peak resolution.

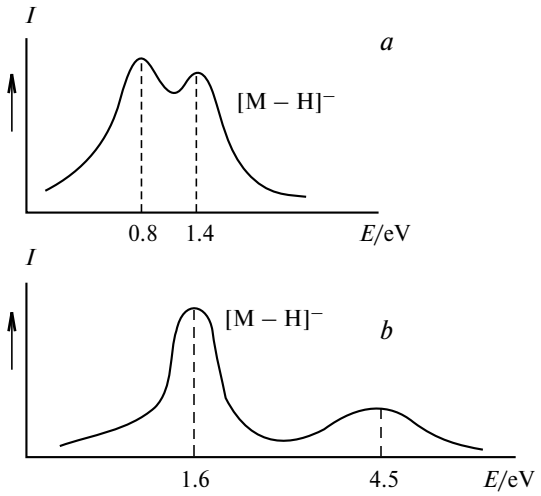


Fig. 1. Intensities of $[M - H]^-$ negative ions in the mass spectra of uracil (**1**) (*a*) and its derivative **9** (*b*) at a ion source temperature of 40 °C.

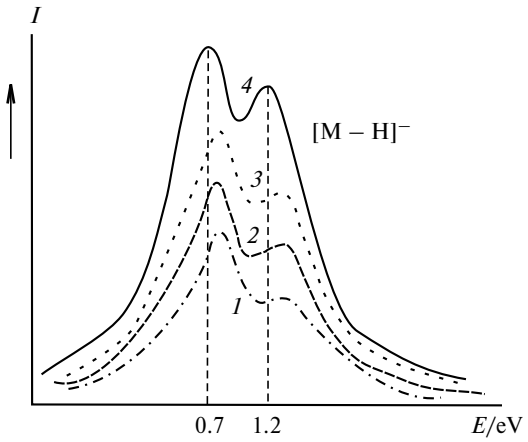


Fig. 2. Intensities of $[M - H]^-$ negative ions in the mass spectra of uracil (**1**) at ion source temperatures of 40 (*1*), 70 (*2*), 100 (*3*), and 140 °C (*4*).

tachment of the H atom from the N atom and from the OH group of the enol form, respectively (Fig. 1). This is evidenced by the mass spectrum of compound **9** (formation of the enol form of this compound is blocked due to the presence of substituents at the nitrogen atoms). The mass spectrum of compound **9** has $[M - H]^-$ ion peaks only at 1.6 and 4.5 eV.

Since the enol form of uracil is less stable than its diketo form, the percentage of the enol form would be expected to increase with increasing ion source temperature. Hence, we studied the dependence of the yield of $[M - H]^-$ ions on the ion source temperature (Fig. 2). It can be seen that the intensity of the second peak increases and is simultaneously shifted to lower energies with increasing temperature.

Assuming, in accordance with the known data,[3] that the fraction of the enol form of uracil in the gas phase is $\sim 10^{-6}$% at 500 K, the relative formation cross-section of the $[M - H]^-$ ions produced from the enol form should be $\sim 10^6$ times larger than that of the ions generated from the diketo form. This cross-section estimated from the maximum achievable yield of the ions from uracil compared to compounds, whose relative formation cross-sections are known (benzene and nitrobenzene),[10] is 10^{-18}—10^{-17} cm^2.

In this case, the relative formation cross-section of the $[M - H]^-$ ions from the enol form should vary in the range of 10^{-12}—10^{-11} cm^2, which is substantially larger than the gas-kinetic cross-sections ($\sim 10^{-14}$ cm^2). Hence, the fraction of the enol form is, presumably, larger than 10^{-3}% of the amount of the diketo form.

Therefore, two resonance states of the $[M - H]^-$ ions of uracil derivatives produced by resonance electron capture are attributed to the detachment of the hydrogen atom from the nitrogen atom of the diketo form (first peak) and from the oxygen atom of the enol form (second peak). The percentage of the enol form in the gas phase is $\sim 10^{-3}$%.

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