

LETTERS
TO THE EDITOR

Keto-Oxy Tautomerism

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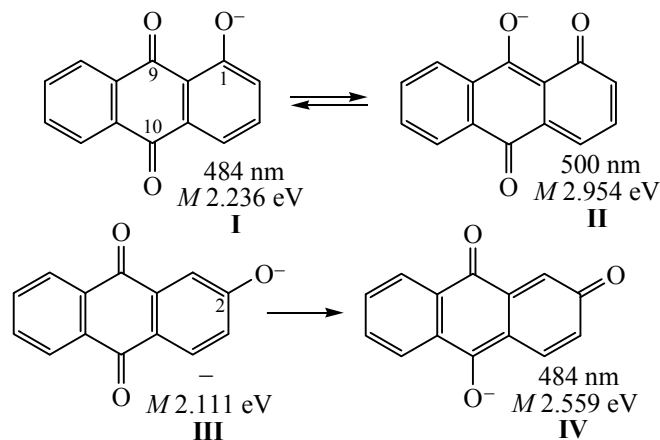
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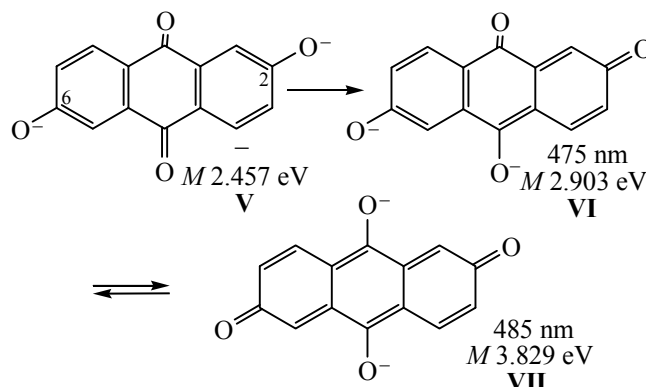
Tautomeric transformations is a very well known phenomenon in organic chemistry and new types of them are now and then reported. One of the most known is the keto-enol tautomerism. On the other hand, the reaction of deprotonation of hydroxysubstituted quinones with the formation of the corresponding oxysubstituted derivatives is of large theoretical and practical importance, especially in the chemistry of natural compounds and analytical chemistry.

We have found that oxysubstituted quinones with conjugated carbonyl and oxy groups show tautomerism connected with the negative charge transfer from one oxygen atom to another. This type of tautomerism should be called keto-oxy tautomerism. It can be exemplified by tautomerism of 1-oxy- (I) ($n = 2$) and 2-oxy-9,10-anthraquinones (III) ($n = 1$):



The tautomers differ in the position of the long-wave π_i, π^* -band in the electron absorption spectra, which is responsible for the color of the compound, and its structure is determined by comparing the λ_{\max} with the π_i, π^* -transition calculated by methods of quantum chemistry. Most often, tautomers I and II exist in different alkaline solutions separately, and only one of the two π_i, π^* -bands is observed in the experimental spectra [1]. For 2-oxyanthraquinone, the

equilibrium is practically completely biased to tautomer IV and the absorption spectra contain only one π_i, π^* -band [2]. 2,6-Dioxyanthraquinone exists in the form of 6,10-dioxy-2,9-anthraquinone (VI) and 9,10-dioxy-2,6-anthraquinone (VII) rather than the 9,10-quinoid tautomer (V) [2].



Apparently, the predominant existence of the oxysubstituted derivatives in the form of a specific tautomer is determined by their relative stability, which is different in vapor and in solution. For vapor, it is characterized by the energy of atomization ΔH , which is maximum for the 9,10-quinoid tautomers, while in solutions, by the coefficient of solvation M , which for all oxy-9,10-anthraquinones is less than for their tautomers. Therefore, solvation must increase the ability of the oxysubstituted derivatives to tautomerization.

The examples shown are indicating that the traditional notions on the structure of oxysubstituted derivatives of 9,10-anthraquinones should be revised.

We believe that the keto-oxy tautomerism is as widely spread as the keto-enol tautomerism.

REFERENCES

1. Fain, V.Ya., Zaitsev, B.E., Ryabov, M.A., *Zh. Org. Khim.*, 2006, vol. 42, no. 10, p. 1484.
2. Fain V.Ya., Zaitsev B.E., Ryabov M.A., *Zh. Org. Khim.*, 2007, vol. 43, no. 10, p. 1460.