

ON THE INFLUENCE OF UV-IRRADIATION ON THE KETO-ENOL EQUILIBRIUM
OF ETHYLACETOACETATE IN SOLUTION

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Keto-enol tautomerism has been widely investigated in recent years. Several factors influencing the keto-enol equilibrium have been studied^{1,2,3}.

The present study, limited to the cyclohexane solutions of ethylacetoacetate, attempts to elucidate the influence of UV-irradiation on the keto-enol equilibrium.

Comprehensive studies of the electronic spectra of ethylacetoacetate in various solvents have been made by many authors^{4,5}. It has been established that the strong K-band at $245m\mu$ is strictly limited to the enol form of this compound. The presence of an absorption maximum in this region of the UV spectrum

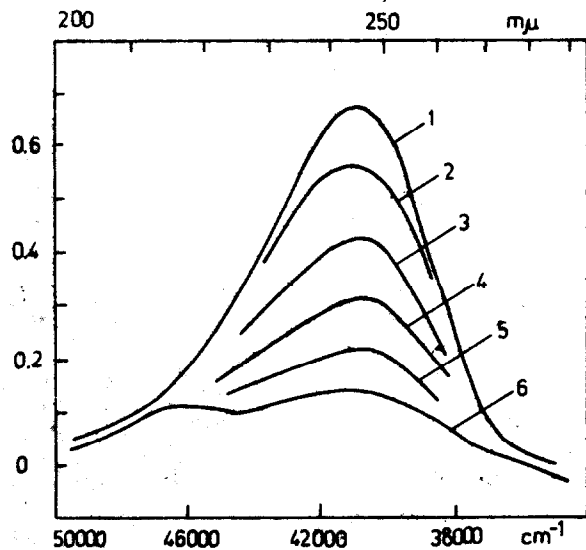


Figure 1

of ethylacetoacetate is sufficient to allow a spectrophotometric assay of the keto-enol ratio in the investigated solutions during the UV-irradiation. Irradiation of a 1.98×10^{-3} , 1.50×10^{-3} and 0.55×10^{-3} mole/l cyclohexane solutions of ethylacetoacetate led to an efficient decrease of enol form. Figure 1 shows the change of the intensity of the absorption band at $245m\mu$ as a result of the irradiation of 1.50×10^{-3} mole/l solution with a Hanau-SRU 300 W

lamp in a quartz glass apparatus. The decrease of the enol form is proportional to the time of irradiation. The results for three series of experiments are shown in Figure 2.

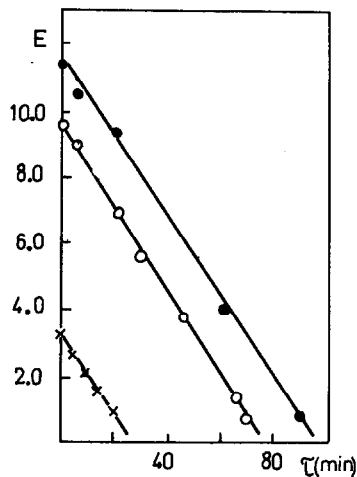


Figure 2

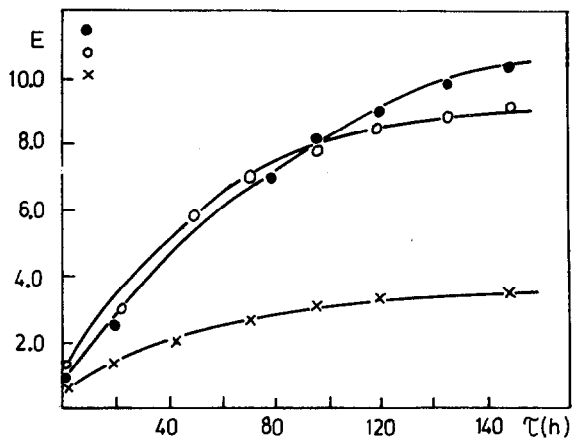


Figure 3

A linear relationship between the concentration of the enol form and the time of irradiation was observed for all irradiated solutions.

The irradiated solutions were investigated spectrophotometrically over a long period of time (170 hours). As can be seen from Figure 3 there exists a gradual restoration of the enol form. The final concentrations of the enol are equal to the respective initial concentrations, obtained before the irradiation.

The observed infrared spectra of 9.49×10^{-3} mole/l cyclohexane solution of ethylacetoacetate before (Fig.4a) and after (Fig.4b) UV-irradiation are given in Figure 4.

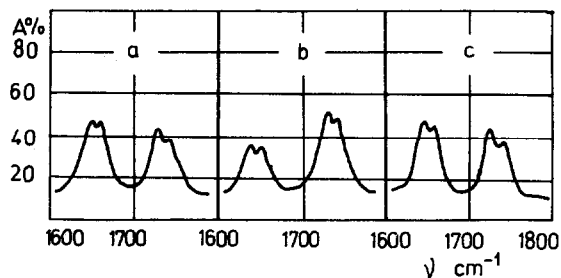
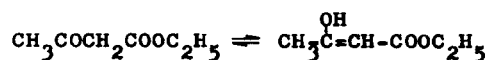


Figure 4

The frequencies in $1720-1740 \text{ cm}^{-1}$ region are assigned to the keto form⁶.

Bellamy⁷ pointed out that two bands in 1630-1650 cm^{-1} region are characteristic of the enol form. As can be seen from Figure 4-b, the UV-irradiation led to the substantial decrease of the enol form related with increasing of the keto form. After 24 hours there exists a restoration of the enol (Fig.4-c).

These results indicate clearly that the UV-polychromatic irradiation causes a very strong displacement of the equilibrium



to the keto form. In the chosen concentration range it seems that the degree of the observed displacement does not depend on the initial enol concentration and depends only on the quantity of the light quanta which fall into the irradiated solution. This quantity was determined by using uranyl oxalate actinometer. The obtained value is 6.37×10^{16} quanta/ml.min.

It can be emphasized that the effect of the UV-irradiation on the keto-enol equilibrium is reversible. There is no experimental data for any presence of photolytic decomposition of ethylacetoacetate.

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