EFFECT OF U.V. IRRADIATION ON THE BASE-CATALYZED ENOLIZATION OF ETHYL ACETOACETATE IN SOLUTION

P. MARKOV

Department of Organic Chemistry, University of Sofia, Sofia (Bulgaria)

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Summary

The base-catalyzed enolization of u.v. irradiated solutions of ethyl acetoacetate has been studied. It was shown that the repeatedly performed photoketonization results in a gradual increase of the rate of the reverse process (enolization), when triethylamine was used as catalyst. The enolization is a first order reaction with respect to the keto form. The rate constant depends strongly on the structure of the catalyst.

Introduction

As an extention of our studies on the photoinduced keto—enol transformations [1 - 5] the present paper investigates the influence of u.v. irradiation on the catalytic effect of some aliphatic amines towards the enolization of ethyl acetoacetate in hexane solutions.

Experimental

Ethyl acetoacetate was carefully rectified prior to use to a 99.9% purity. The various liquid catalysts used in the kinetic runs were purified by distillation shortly before use. Hexane was of Merck Spectroscopic Grade. The concentrations of solutions investigated are given in the text. In order to check the purity of the quartz glass cell, blank kinetic runs were made before starting the irradiation of the experimental sample.

The equilibrated (105 days) hexane solutions of ethyl acetoacetate, containing the respective quantity of the basic catalyst were irradiated with Hanau 300 W medium pressure mercury arc lamp in a quartz glass cell with path length 10 mm under standard conditions. As a result of the photoketonization [1 - 3], the concentration of the enol form was fixed at 0.2×10^{-4} mol/l shortly before starting the respective kinetic run. The light quanta, falling into the quartz cell, were determined by using a uranyl oxalate actinometer. The value obtained was 1.12×10^{15} quanta ml^{-1} s^{-1}.

TABLE 1[a]

Influence of u.v. irradiation on the rate of enolization of ethyl acetoacetate in hexane solutions (1×10^{-4} mol/l) in the presence of various basic catalysts (5×10^{-7} mol/l)

Photo-ketoni-zation	$k \times 10^4$ (s^{-1})						
	n-PrNH$_2$	n-BuNH$_2$	n-AmNH$_2$	i-PrNH$_2$	Triethyl-amine[b]	Piperidine	Pyridine
1	1.04	2.54	3.62	0.08	0.10	2.80	0.14
2	1.03	2.57	3.61	0.08	0.23	2.77	0.15
3	1.06	2.61	3.57	0.07	0.70	2.82	0.14
4	1.05	2.56	3.60	0.08	1.27	2.80	0.13
5	1.04	2.63	3.54	0.09	1.84	2.76	0.15
6	1.05	2.71	3.64	0.10	2.63	2.80	0.15
7	1.02	2.64	3.59	0.08	3.47	2.79	0.14
					1.83[c]		

[a]The measurements were made using one sample for each catalyst, after successive 20 min u.v. irradiations (photoketonization).
[b]Concentration 0.5×10^{-4} mol/l.
[c]After one month stay of the sample at 0 °C.

The enolization was catalyzed by the addition of a basic compound (see Table 1). The concentrations of enol form, C_e, were obtained from the respective absorbances, A, at 246 nm. The absorption maximum at this wavelength is strictly limited to the enol form of ethyl acetoacetate [6]. The molar extinction coefficient is 10,700 [7]. The u.v. absorption spectra were measured on a Specord UV–VIS spectrophotometer.

All kinetic runs were repeated after a new photoinduced shift of the keto–enol equilibrium towards the keto form. The existence of a fair reproducibility of the kinetic data has been firmly established with the only exception of triethylamine used as a catalyst (see the discussion). The method of least squares was used to obtain the best fitting of the experimental data to the function (1).

Results and Discussion

It was found that the rate of non-catalyzed enolization of ethyl aceto-acetate in hexane was extremely low when the solution was kept in a quartz vessel of high purity. In our experimental conditions the keto–enol equilibrium was reached within several months (105 days). It is evident that under these conditions the thermodynamic ratio between the two tautomers was reached virtually in absence of catalyst.

The experimental data obtained in the case of base-catalyzed enolization satisfied function (1) which is a solution of the rate equation for first order kinetics:
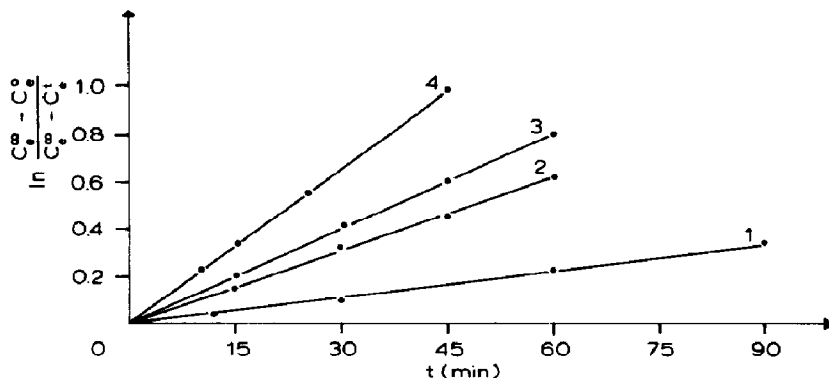
Fig. 1. Plot of $\ln[(C_e^\infty - C_e^\circ)/(C_e^\infty - C_e^t)]$ vs. t at different concentrations (C_b) of the catalyst (n-amylamine): 1, 0.079×10^{-7}; 2, 0.316×10^{-7}; 3, 1.300×10^{-7}; 4, 5.000×10^{-7} mol/l. $C_e = 0.2 \times 10^{-4}$ mol/l; $\lambda = 246$ nm; cell length, 10 mm.

$$\ln \frac{C_e^\infty - C_e^\circ}{C_e^\infty - C_e^t} = kt \qquad (1)$$

C_e° and C_e^∞ denote the initial and equilibrated concentrations of the enol form. C_e^t is the concentration t seconds after starting the kinetic run. Some earlier investigations indicate that the non-catalyzed enolization of ethyl acetoacetate [8] and some β-diketoesters [9] is a first order reaction.

Plots of $\ln[(C_e^\infty - C_e^\circ)/(C_e^\infty - C_e^t)]$ against t at different concentrations of the basic catalyst (n-amylamine) show the existence of a good linear relationship (Fig. 1).

The constant k consists of the sum of the rate constants of the forward (k_1) and reverse (k_{-1}) reactions, if the prototropic change is not catalyzed:

$$CH_3COCH_2COOC_2H_5 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CH_3\overset{OH}{\overset{|}{C}}=CHCOOC_2H_5$$
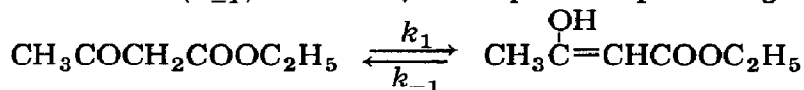
As shown by Takemura and Baba [10] in the case of base-catalyzed isomerization of anthrone, k values obtained vary with the base concentration C_b. From the data, presented in Fig. 1, it can be seen that a similar relationship exists in the case considered by us.

The influence of u.v. irradiation on the rate of enolization of ethyl acetoacetate was studied in the presence of the following base catalysts: n-propylamine, n-butylamine, n-amylamine, isopropylamine, triethylamine, piperidine and pyridine. The observed rate constants (k) of the enolization in the u.v. irradiated hexane solutions of ethyl acetoacetate are presented in Table 1.

The most striking feature of Table 1 is that as a result of repeatedly performed photoketonization, the reverse process rate gradually increases when triethylamine is used as a catalyst (Fig. 2). The initial k value is 15 times smaller than that obtained after six prototropic transformations (photoketonization–enolization).
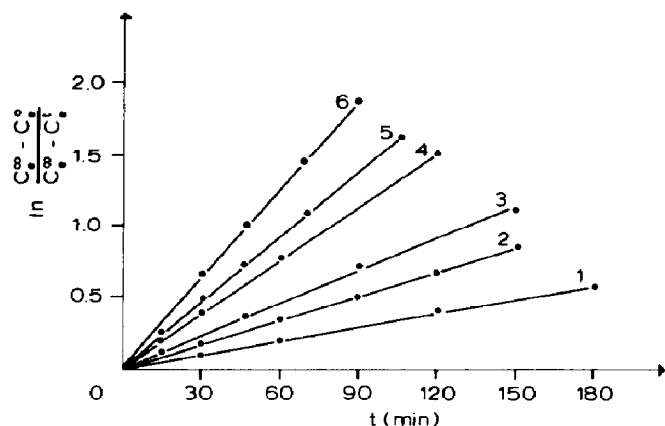
Fig. 2. Plot of $\ln[(C_e^\infty - C_e^o)/(C_e^\infty - C_e^t)]$ vs. t after successive 20 min irradiations. Basic catalyst, triethylamine ($C_b = 0.5 \times 10^{-4}$ mol/l).

The repeatedly irradiated hexane solution of ethyl acetoacetate and triethylamine ($k = 3.47 \times 10^{-4}$, Table 1) was allowed to stay at 0 °C for a month. As a result, a diminution of the catalytic effect of triethylamine was observed ($k = 1.83 \times 10^{-4}$). A further irradiation of the sample restores the catalytic activity of the base used.

It should be pointed out that the separate irradiation of a hexane solution of triethylamine before use as a catalyst leads to a minor acceleration of the rate of enolization in spite of the long duration of the irradiation (5 h). This observation is interesting since it means that only the simultaneous u.v. irradiation of the enolizable compound and triethylamine leads to a significant increase of the basic catalyst activity.

It can be assumed that under the influence of u.v. light, triethylamine undergoes a chemical change and the observed acceleration is due to the newly formed products. As it has already been shown [11], the irradiation causes a photochemical reaction between triethylamine and tetrachloromethane. However, in the case considered here such a possibility can be excluded because of the use of an inert solvent. Such a conclusion is supported by the fact that prolonged irradiation of triethylamine alone does not lead to a significant increase of the catalytic effect. On the other hand, the total reversibility of the photoinduced shift indicates the lack of an irreversible interaction between catalyst and enolizable compound.

The accelerating effect of u.v. irradiation occurs only in the case when tertiary amine is used as catalyst. As can be seen from the data summarized in Table 1 in the remaining cases there is no change in the rate of enolization. The marked difference from the behaviour of ethyl acetoacetate--triethylamine system remains unexplained at present.

The experimental results (Table 1) proved unequivocally that the catalytic effect of the base increases with an increase in the length of the carbon chain of the respective amine, in spite of the fact that their basicities are nearly the same the only exception being pyridine. So far as there are

no important differences in the electronic and steric characteristics of the amines used, little can be said concerning the nature of the observed dependence between the length of the carbon chain and the catalytic activity.

The branching of the carbon chain leads to a substantial decrease of the activity of the basic catalyst. n-Propylamine was found to be about 13 times more effective than isopropylamine. Triethylamine also possesses very low catalytic ability. This prompted us to suggest that the steric requirements of the process of base-catalyzed enolization are very important. The greater catalytic effect of n-butylamine as compared to triethylamine is explained by the presence of two hydrogen atoms instead of the bulky ethyl groups bonded to the nitrogen atom.

References

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