Ionization and isomerization of acetylacetone in mixed solvents

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The isomerization and ionization of acetylacetone in two-component systems was measured. The influence of medium on both equilibria is discussed on the basis of the idea of changes in solvation of particles.

Исследовалась кинетика изомеризации и ионизации ацетилацетона в двухкомпонентных растворителях. Обсуждается влияние растворителя на оба равновесия на основе представлений об изменениях сольватированности частиц.

The use of acetylacetone and other β-diketones as ligands [1] arouses interest in the study of their isomerization and ionization equilibria because these equilibria also affect the equilibria relative to the formation of metal complexes. Unfortunately, only small attention has been paid to this problem in literature. The ionization constants of acetylacetone in water [2—5] and in the water—dioxan system [6] were occasionally investigated. The structure and the pertinent tautomeric equilibrium of acetylacetone were investigated by the use of X-ray structural analysis [7], electron diffraction [8, 9], and NMR, UV or IR spectrometry [10—14]. In agreement with literature [15], Scheme 1 may be written for acetylacetone on the basis of the known isomerization and ionization.
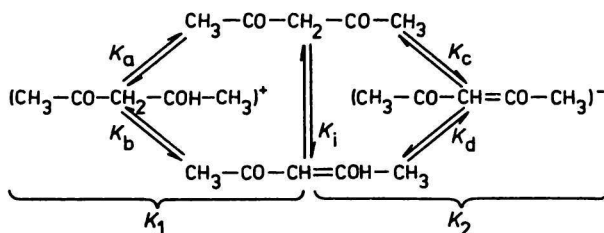
Scheme 1

The ionization constant K_2 is governed by eqn (1) while the isomerization constant K_i obeys eqn (2) [16]. Hence it follows that the constants K_c and K_d are easily available from the experimental data.

$$1/K_2 = 1/K_c + 1/K_d \qquad (1)$$

$$K_i = K_d/K_c = [keto]/[enol] \qquad (2)$$

The relations among K_1, K_a, K_b, and K_i are known, too [16]. However, they are not necessary for understanding the following text. The ionization of ketones proceeds very rapidly [14, 15] and catalyzes the establishment of isomerization equilibrium in the same manner as the formation of complexes [17]. For this reason, both isomers are to be separated [18] only under special conditions and in the absence of acids and bases.

Experimental

The experiments were carried out with anal. grade acetylacetone (Reakhim, Moscow). It was two times distilled and the fraction boiling at 194 °C was used. The ionic strength was kept constant by means of tetramethylammonium chloride (anal. grade reagent, Fluka).

The ^1H NMR spectra were measured with an instrument Varian T-60 (60 MHz). The proportion of the keto form and enol form was determined from the intensity of signals of the methyl groups with a precision of $\pm 5\%$.

A spectrophotometer Pye—Unicam SP 8-100 was used for recording the spectra of acetylacetone solutions ($c = 4 \times 10^{-5}$ mol dm^{-3}) in the ultraviolet region by using different solvents at (25 ± 0.1) °C.

The ionization constant of acetylacetone was measured spectrophotometrically in buffer solutions. The absorbance of samples of different pH values was measured at $\lambda = 291$ nm and the results were used for calculating pK_2 according to the equation

$$pK_2 = pH - \log \frac{A - A_a}{A_b - A} \qquad (3)$$

where A_a, A_b, and A are absorbance of the solution containing neutral molecules, absorbance of the solution containing anions, and absorbance of the solution containing anions as well as molecules of acetylacetone, respectively. The pK_2 value thus obtained was extrapolated to the zero ionic strength by using the expression

$$pK_2^\circ = pK_2 + \frac{\sqrt{I/(unit\ I)}}{1 + \sqrt{I/(unit\ I)}} \qquad (4)$$

The pH values were measured with a pH-meter PHM-64 Radiometer (Copenhagen) by means of a glass electrode and a silver/silver chloride electrode filled with saturated or 0.1 mol dm^{-3} solution of NaCl in the same solvent in which acetylacetone was dissolved.

Table 1

Isomerization constants, relative deviations of the measured and calculated absorbances (%) and constants pK_2^o, pK_c^{pKd} measured at 25 °C

System	$w(H_2O)/\%$	K_i	Relative deviation of absorbance/%		pK_2^o	pK_c	pK_d
Water—methanol	100	7.13	-12^a		8.95	8.89	8.04
	80	3.78	$+14$		9.59	9.47	8.99
	60	2.16	$+11$		9.87	9.70	9.37
	40	1.25	$+4$		10.10	9.74	9.65
	20	0.74	-5		10.54	10.17	10.30
	10	0.64	-6		10.95	10.54	10.74
	0	0.57	—		—	—	—
Water—2-propanol	80	2.77	$+14$		9.25	9.12	8.67
	50	0.90	$+8$		9.93	9.61	9.65
	30	0.56	$+3$		10.36	9.91	10.17
	10	0.29	-14		11.37	10.72	11.26
Water—1,4-dioxan	90	4.89	-7		9.26^b	9.18	8.49
	80	3.41	$+26$		9.49^b	9.39	8.81
	70	2.47	$+4$		9.77^b	9.65	9.16
	60	1.79	-4		10.10^b	9.92	9.64
	50	1.39	-8	10.4	10.53^b	10.31	10.13
	30	0.84					
	10	0.48					
Water—DMSO	80	7.13	—		—	—	—
	60	2.56	—		—	—	—
	40	1.90	—		—	—	—
	20	1.35	—		—	—	—
	0	0.74	—		—	—	—

a) For the water—2-propanol system found — 17 % and for the water—1,4-dioxan system found — 12 %; *b*) taken from Ref. [6].

The electrode system was dipped for 20 h before measurement in the used solvent and subsequently calibrated with the buffer solutions recommended in literature [19, 20]. The error of the data thus obtained is ± 0.02 pH unit [21].

Results and discussion

The measurements of the ^{1}H NMR spectra of acetylacetone gave data about the proportion of both isomers in solution. The isomerization constants K_i defined by eqn (2) which were obtained from these data are presented in Table 1.

It is obvious with respect to the definition of K_i and data in Table 1 that the relative proportion of the enol form increases with concentration of the organic component in the solvent. In order to express the dependence of isomerization constant on medium, we usually use some empirical equations [22] in which the dependence of pK_i on several experimental properties of solvent is respected. This approach is consistent with the well-known experience according to which the isomerization constant is not a simple function of single measurable physical parameter. Our experiments are in agreement with this observation. The attempt to correlate pK_i with the function $\theta(\varepsilon)$ [23] resulted in a nonlinear relationship though a linear relationship was obtained in some cases according to literature [24]. Similarly, the dependence of pK_i on E_T [25] was nonlinear for the systems water—methanol and water—2-propanol and linear only for the water—dioxan system (Fig. 1). In this relation, it is worth noticing that the pK_i value of the ethyl ester of acetoacetic acid as a function of Z is also nonlinear [26].
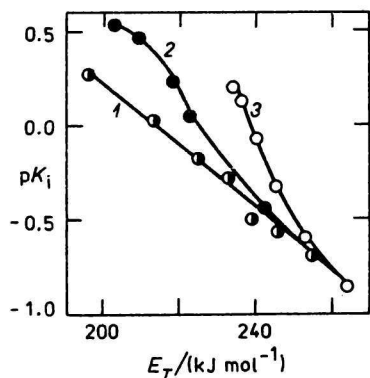

Fig. 1. Variation of pK_i with E_T in different systems:
1. water—dioxan; 2. water—2-propanol;
3. water—methanol.

The measurement of ionization constant enables us to determine to which degree both forms participate in light absorption. On the basis of a particular experiment, it was ascertained that acetylacetone followed the Lambert—Beer law in all solvents with a precision of 1%. Provided the molar absorption coefficients of both isomers are constants and do not change with solvent as assumed in paper [12], we are able to calculate the molar decadic absorption coefficients from the values of absorbance, total concentration of acetylacetone, and isomerization constant. On the basis of the method of least squares, it was found $A = 9708\,c_E/(\text{mol dm}^{-3}) + 77\,c_K/(\text{mol dm}^{-3})$ for the water—methanol system, $A = 9243\,c_E/(\text{mol dm}^{-3}) + 61\,c_K/(\text{mol dm}^{-3})$ for the water—2-propanol system, and $A = 9746\,c_E/(\text{mol dm}^{-3}) + 82\,c_K/(\text{mol dm}^{-3})$ for the water—dioxan system. The symbols c_E and c_K stand for concentrations of the enol form and of the keto form, respectively.

The differences between the found and calculated absorbances in percentage are given in Table 1 (the experimental value corresponds to 100 %). Irrespective of the fact that the calculation does not involve the values of substance absorbance in pure organic solvents which should still more impair the results, it is obvious that the experimental and theoretical results are not consistent. The differences may be due to a change in molar absorption coefficients caused by different solvents as well as to inaccuracy of the ^{1}H NMR method. The differences between our values of K_i and the values found in literature [12] may originate in those facts.

Eqn (3) was used for obtaining the pK_2 values with an error less than $\pm 0.04\ pK$ unit except for the system with 50 mass % of dioxan where the measured pK_2 value is subject to an error of $\pm 0.1\ pK$ units. The error of pK was still greater in solutions with higher concentrations of dioxan. The validity of the Lambert—Beer law for the ionized as well as nonionized form of the substance was verified by a particular experiment. Therefore the errors of pK may be due to the existence of other equilibrium which has not been taken into account in deriving eqn (3). This equilibrium may involve dimerization, homoconjugation or other processes made possible by poorly polar solvent. Thus the system becomes obscure because there are not sufficient experimental data for identifying the additional equilibrium. For this reason, the pK_2^o value is quoted in Table 1 only for 50 % dioxan, which is in agreement with literature in the range of the error of measurement [6]. As for the water—dimethyl sulfoxide system, the values necessary for correlation with pK are not tabulated and therefore the pK values in this medium were not measured. Table 1 also contains pK_c and pK_d calculated from eqns (1) and (2). These data refer to C-acid (pK_c) and O-acid (pK_d) and enable us to investigate the influence of medium on ionization of different types of acids if all other parameters (size of molecule, charge, etc.) have been preserved. The influence of medium on ionization is to be expressed by a few ways among which a comparison of ΔpK seems to be the most convenient for our purpose. A comparison of ΔpK of the sample with ΔpK of the standard enables us to conceive an idea of the relative influence of medium on ionization. It is advantageous to choose a substance the ionization of which is known with sufficient precision to be the standard. In this connection, acetic acid the pK value of which has been taken from literature [27, 28] seems to be appropriate for serving as standard. A comparison of the ΔpK values of both isomers with the ΔpK value of acetic acid is represented in Figs. 2 and 3. It is obvious that ΔpK_d depends on $\Delta pK(CH_3COOH)$ in the same manner as ΔpK of carboxylic acids with a more voluminous anion [28]. The dependence of ΔpK_c on $\Delta pK(CH_3COOH)$ is, however, much less significant and much more curved.

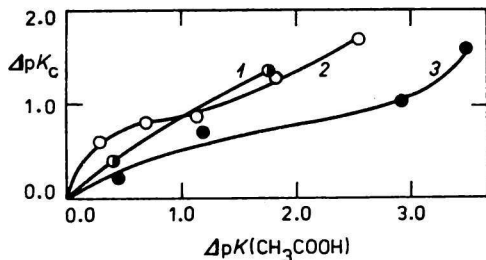The relationship between ionization constant and isomerization constant is

Fig. 2. Variation of ΔpK_c with
$\Delta pK(CH_3COOH)$ in different systems:
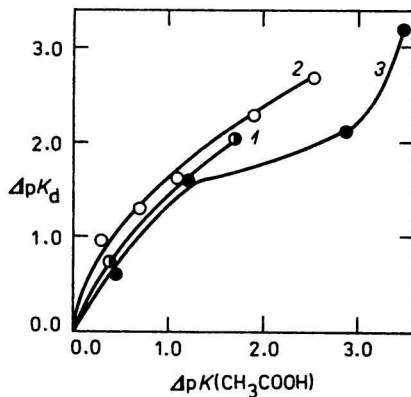*1.* water—dioxan; *2.* water—methanol;
3. water—2-propanol.

Fig. 3. Variation of ΔpK_d with
$\Delta pK(CH_3COOH)$ in different systems:
1. water—dioxan; *2.* water—methanol;
3. water—2-propanol.

described by eqn (*2*). According to this equation, the isomerization equilibrium is always shifted to the side of that isomer which is a weaker acid. In order to comprehend this effect, we can start from the idea of solvation of particles according to which the more firmly solvated is a particle in solution, the more stable it is. The acetylacetate anion as well as the hydrogen cation comes into existence by ionization of both keto and enol form. Therefore the difference in pK of both isomers must be in relation to different solvation of neutral molecules. The pK values found in water lead to the idea that the keto form is more firmly solvated in water than the enol form because its ionization equilibrium is less shifted in the sense of the ionized portion than the ionization equilibrium of the enol form. The keto form is therefore a weaker acid. The stability of both forms is also in relation with isomerization equilibrium. It results from preceding considerations that the more firmly solvated keto form is prevailing in water over the more weakly solvated enol form and the K_i value ought to be greater than one. The experimental data in Table 1 confirm the rightness of this reasoning.

A passage from the aqueous medium into a mixed solvent reduces the solvation of ions, owing to which pK shifts towards higher values. The shift in pK is also influenced by a change in solvation of the neutral molecule. Of course, the solvation of molecules and ions is specific for every organic cosolvent. Thus the more the decrease in stability of the solvate of ions is accompanied by a decrease in stability of the solvate of molecules, the smaller is the change in pK caused by the medium. The data in Table 1 enable us to draw a conclusion that the change in stability of the solvate of the enol form due to the passage from water to a mixed solvent is less than the change in stability of the solvate of the

keto form. Of course, a considerable decrease in stability of the solvate of keto form brings about a considerable change in K_i in the sense of smaller values. This consideration is also consistent with the data in Table 1. Thus it is obvious that the idea of the solvation of particles and their changes is appropriate for interpreting not only the qualitative change in pK with medium [29, 30] but also the change in isomerization constants due to the medium and represents the basis for complex comprehension of both phenomena, *i.e.* isomerization and ionization.

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