STUDY OF THE TAUTOMERISM OF 2-ACETYL-1-CYCLOPENTANONE
AND 4-ACETYL-3-THIOPHANONES

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In a study of the tautomerism of N-alkyl-3-carbomethoxy-4-piperidones, we discovered that the Meyer equation is not fulfilled, if acetoacetic ester is taken as the standard substance [1]. The nitrogen atom in tertiary amines is capable of forming strong hydrogen bonds [2]; therefore, deviations from the Meyer equation for N-alkyl-3-carbomethoxy-4-piperidones are explained by different solvation of the nitrogen atoms in the ketone and enol forms on account of a difference in their conformations [1]. In this work we discuss the tautomerism of 2-acetyl-1-cyclopentanone (I), 4-acetyl-3-thiophanone (II), and 5,5-dimethyl-4-acetyl-3-thiophanone (III). These compounds can be enolized in two directions, and their equilibrium is characterized by four constants:

\[ K_{TS} = \frac{e'_{TS}}{e_{TS}}, \quad K_{TS} = \frac{e''_{TS}}{e_{TS}}, \quad K_{TS} = \frac{e'_{TS}}{C_{TS}} \quad \text{and} \quad K_{TS} = \frac{e''_{TS}}{C_{TS}}, \]

where \( e'_{TS} \) and \( e''_{TS} \) are the concentrations of the two enol forms, while \( C_{TS} \) is the concentration of the keto form of the tautomer \( T \) in the solvent \( S \).

Just as in the case of N-alkyl-3-carbomethoxy-4-piperidones, the keto and enol forms (I)-(III) have different conformations [3, 4]. However, in contrast to the nitrogen atom in tertiary amines, the sulfur atom in sulfides is weakly solvated [5]. The C - S bonds are considerably longer than the C - N bonds, and the steric possibilities of solvation of the sulfur atom in sulfides (two unshared electron pairs) are considerably better than for the tertiary nitrogen atom (one unshared pair). Therefore, the ratios of the corresponding equilibrium constants for (I)-(III) to the equilibrium constant for the ethyl ester of cyclopentane-1-one-2-carboxylic acid (IV) and acetylacetone (V), which are taken as the standard substances, will be the same for different states:

\[ \frac{K_{T1S}}{K_{T2S}} = \frac{K_{T1S}}{K_{T2S}} = \ldots = \frac{K_{T1S}}{K_{T2S}} = a. \]

where \( T_2 \) is the standard substance (IV) or (V), while \( T_1 \) is the corresponding equilibrium state of (I)-(III). In this case, the dependence of the ratio of the summary equilibrium constant of (I)-(III) to the equilibrium constant of (IV) and (V) on the nature of the state is of interest. Let us write such ratios for the tautomers \( T_1 \) and \( T_2 \) in the solvents \( S_1 \) and \( S_2 \). Considering that \( K_{T1S} = K_{T1S} + K_{T1S} \), we find

\[ \frac{K_{T1S} + K_{T1S}}{K_{T1S}} = \frac{K_{T1S} + K_{T1S}}{K_{T1S}}. \]

Using Eq.(1), we obtain
which, with simplification, gives

\[
\frac{K_{T,S_1}}{K_{T,S_2}} = \frac{K_{T,S_1}}{K_{T,S_2}}.
\]

(4)

Replacing the equilibrium constants in Eqs. (4) by the concentrations of the ketone and enol forms, we find

\[
\frac{c_{T,S_1}}{c_{T,S_2}} = \frac{c_{T,S_1}}{c_{T,S_2}}.
\]

(5)

The ratio of the summary equilibrium constant of (I)-(III) to the equilibrium constant of (IV) and (V) is the same in a number of states, if the constant of enol – enol equilibrium of (I)-(III) is the same in these states. The latter is possible if the enol – enol equilibrium is strongly shifted in the direction of the corresponding enol form or when the difference in the solvation of the enol forms is small. Inconstancy of the ratio indicates the presence of a substantial amount of both enol forms in the equilibrium of (I)-(III) and substantial differences in the solvation of the enol forms. Thus, the ratio of the summary equilibrium constant of (I)-(III) to the equilibrium constant of (IV) and (V) can be used to study the enol – enol equilibrium (I)-(III). In this work, the summary equilibrium constants (I)-(III) were replaced by the quantities equivalent to them

\[
M_{TS} = \frac{\varepsilon_{T,S}}{\varepsilon_{T,S_0}}
\]

(6), where \(\varepsilon_{T,S}\) is the molar extinction coefficient of the ketoenol T in the solvent S, \(\varepsilon_{T,S_0}\) is the molar extinction coefficient of the ketoenol T in the standard solvent \(S_0\). It is known [7, 8] that the absorption maximum of cyclic \(\beta\)-ketoesters depends on the conformation of the ring. However, this dependence is not so substantial as to expect the appearance of two enol maxima in the UV spectra of (I)-(III). Actually, there is one enol maximum in the UV spectrum of (I)-(III), only somewhat broader than in the spectra of acetylacetone. The molar extinction coefficients of the enols of cyclic \(\beta\)-ketoesters depend weakly on the conformation of the ring [9]. Therefore, the absorption of the maximum in the UV spectra of (I)-(III) was taken as the characteristic of the summary enol content in them.

Data on the UV spectra and values of \(M_{TS}\) of compounds (I)-(III) in solutions are presented in Table 1. The limits within which \(\varepsilon_{T,S}\) is reproducible and the errors due to this in the determination of \(M_{TS}\) are indicated. Table 2 presents the ratios of \(M_{TS}\) for compounds (I)-(III) and (IV), (V) and the limits within which they were determined. The values of \(M_{TS}\) for (IV) and (V) were taken from [6]. From Table 2 it follows that the ratios are constant within the limits of the experimental error for acetonitrile, alcohols, and dimethylformamide. It is known from the literature [10] that in the enol – enol equilibrium (I), both enol forms are present in substantial amounts. Consequently, the constancy of the ratios of \(M_{TS}\) of (I) and (IV), (V) in these solutions is due to the uniform solvation of the enol forms. The enol – enol equilibrium of (II) and (III) may be shifted in the direction of one form [11]. The change in the ratio in dioxane may be associated with an error in the determination of \(\varepsilon_{T,S}\) on account of the low rate of establishment of the equilibrium. In the UV spectra of (I)-(III) in dimethyl sulfoxide, a shift of the absorption maximum in the short-wave direction is observed (see Table 1). For acetyl acetone, there is no such shift. Possibly there are some sort of special interactions of the enols (I)-(III) with dimethyl sulfoxide, which lead to fulfillment of Eq. (1).

In [6] it was shown that if the Meyer equation is fulfilled for two ketoenols, then the molar extinction coefficient of the enol of one of the ketoenols can be determined using the equation

\[
\varepsilon_{OT} = \frac{\varepsilon_{T,S_1} \varepsilon_{T,S_2} (\varepsilon_{T,S_1} - \varepsilon_{T,S_2}) + n \varepsilon_{T,S} \varepsilon_{T,S_1} (\varepsilon_{T,S} - \varepsilon_{T,S_1})}{n (\varepsilon_{T,S} \varepsilon_{T,S_1} - \varepsilon_{T,S} \varepsilon_{T,S_2})} = A/n + B,
\]

(6)

where \(\varepsilon_{OT}\) is the molar extinction coefficient of the enol of the ketoenol T; \(\varepsilon_{T,S}\) is the molar extinction coefficient of the ketoenol T in the solvent S; n is the coefficient in the equality \(\varepsilon_{OT} = n \cdot \varepsilon_{OT_1}\). Ideas of the errors in the determination of the coefficient A at 1/n and the free factor B in Eq. (6) can be obtained if A and B are determined for all possible combinations of states, also using the standard state.

We used Eq. (6) to determine the molar extinction coefficient of the enol mixture (I)-(III). (IV) was taken as the standard tautomer. In this case Eq. (6), written relative to \(\varepsilon_{OT}\) for (I)-(III), takes the form

\[
\varepsilon_{OT} = -A (1/n) + B, \quad \text{where } B > A.
\]

The values of the coefficients A and B for all possible combinations of states in which the Meyer equation is fulfilled are cited in Table 3. In determining the average values, the