

KETO-ENOL TAUTOMERIZATION RATES OF ACETYLACETONE IN MIXED AQUEOUS MEDIA

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Abstract—The kinetics of keto-enol tautomerization of acetylacetone was studied in mixed aqueous media by u.v. and NMR spectrometries. As an organic component, aprotic (dioxane and acetonitrile) and protic (methanol, ethanol and *t*-butanol) solvents were used. The tautomerization reaction was initiated by the vapor injection method. It is found that an aprotic component does not show any specific effect, while alcohol shows a characteristic effect on both of the reactions of ketonization and enolization. From the results of the composition dependency, the participation order of water and the activation parameters for the reaction, the effect of mixed solvent on the rate is interpreted in terms of the preferential solvation and the association of hydroxylic solvent.

INTRODUCTION

CHEMISTRY of β -diketone has been widely developed today, mostly because of its utility as an organic ligand, e.g. as a powerful extractant in an analytical use. In a series of our research works the role of solvents governing the partition of β -diketones and their metal chelates was clarified[1–3]. However in any course of studying on the detailed mechanism of a complex-formation reaction and a solvent extraction including β -diketones, the keto-enol tautomerism of these reagents must be considered as an essential process. The acid dissociation of β -diketone has been studied in aqueous solution by various techniques[4–6]. While concerned with the solvent effect on the keto-enol tautomerization, a few works on equilibrium constant have appeared[7–9]. It is the purpose of this study to examine the effect of water–organic solvent mixtures on the rate of keto-enol transformation reaction of acetylacetone, which is chosen as a typical and simple compound in a series of β -diketones. Our present interest is focused on the role of water in two elemental processes of mixed media; water–aprotic and water–protic (alcoholic) solvent mixtures.

EXPERIMENTAL

Materials

Acetylacetone obtained commercially was distilled prior to use after washing with ammonia water and drying with anhydrous sodium sulfate. Finally, the portion distilled at 138°C was collected. Organic solvents were purified by ordinary methods[10]. Redistilled water was used. The purity of acetylacetone and organic solvents was examined

by g.c. and u.v. Mixed solvents were all prepared by mixing the weighted portions of pure components.

Kinetics of tautomerization

For all kinetic runs the glass stoppered reaction cell containing 3 ml of mixed solvent was placed in the constant temperature block of the Hitachi 356 spectrophotometer through which water from the HAAKE-FK thermostat was being circulated at $25 \pm 0.02^\circ\text{C}$. The tautomerization reaction was initiated by the vapor injection method as described below. The tautomerization rate was followed by monitoring the subsequent decrease of the absorbance of enol form of acetylacetone at 273 nm just after injecting nearly constant volume (*ca.* 0.6 ml) of the mixed vapor of acetylacetone with the carrier nitrogen gas into the reaction cell. The enol content in the vapor state of acetylacetone was established as 93.3 per cent at 25°C [11]. Dissolution of gaseous acetylacetone is complete immediately after injection. A change in the absorbance which was continuously recorded as a function of time was fairly transformed to the first-order plots in all cases, and the slope gave the experimentally observed rate constants, k_{obs} . As any concentration effect of acetylacetone on the rate was not observed over the range $3.5 \times 10^{-5} - 1.1 \times 10^{-4}$ M, the experiments were performed within this concentration region, usually at *ca.* 8×10^{-5} M.

Determination of enol fractions by NMR

All the NMR data were obtained with the Varian Associates Model A-60 NMR spectrometer equipped with a variable-temperature probe. The enol fraction, *f*, defined as the concentration ratio of the enol form to the total acetylacetone, was determined with a precision of ± 0.02 of enol fraction from the integrated resonance intensity of an appropriate signal, usually the methyl proton signals of enol and keto forms. Before NMR measurement, a sample was allowed to stand over 24hr for equilibration at the measurement temperature. During the measurements the temperature remained constant to within $\pm 1.5^\circ\text{C}$, as indicated by the separation in Hz between two representative peaks in methanol.

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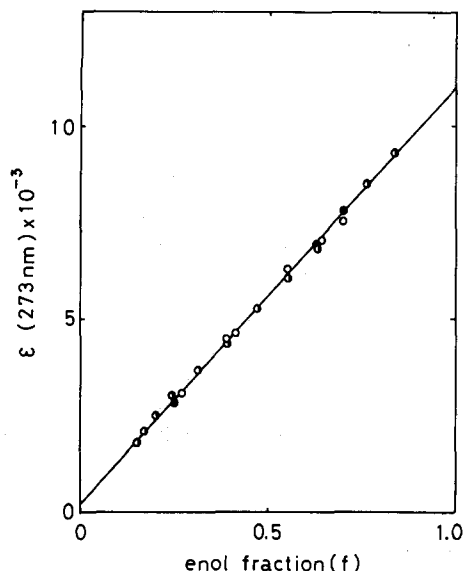


Fig. 1. Apparent molar absorptivity of acetylacetone as a function of enol fraction, 25°C. $\epsilon = 10760 \pm 60)f + (249 \pm 28)$. Organic component: \bullet , dioxane; \circ , methanol; \bullet , ethanol.

Estimation of enol fraction by ultraviolet absorption

Since the NMR method was not applicable to the *t*-butanol–water system due to the interference of the solvent signals, the following method was attempted. That is, the plots of the apparent molar absorptivities of acetylacetone at 273 nm against the enol fractions determined by NMR show good linearity in binary aqueous mixtures of dioxane, methanol and ethanol as shown in Fig. 1. Hence, an instantaneous estimation of the enol fraction in *t*-butanol–water system become capable by knowing only the apparent molar absorptivity. This relationship would be expected to be extended to other solvent systems in which enol and keto forms are major species. From an intercept of Fig. 1, the true molar extinction coefficients of the enol and the keto forms of acetylacetone are estimated as $(1.10 \pm 0.01) \times 10^4$ and 249 ± 28 , respectively.

Temperature effect on the rate

The apparent rate constants of tautomerization were measured in dioxane–water and methanol–water systems at five different temperatures in the range of 5–60°C. The temperature in the cell was monitored by Takara thermister SPD-02-10A accurated to about $\pm 0.2^\circ\text{C}$. To make appropriate corrections for a temperature dependence of keto-enol equilibrium the enol fraction was determined at 0°, 25° and 39°C by NMR.

RESULTS

In Fig. 2 all the observed rate constants are shown as the plots of $\log k_{\text{obs}}$ vs the mole fraction of organic component, X_s . The contribution of organic solvents looks like different substantially in protic and aprotic ones. It appears that decreases of the rate constant are not so remarkable in the alcohol–water mixtures as in the systems containing aprotic solvents. The estimated

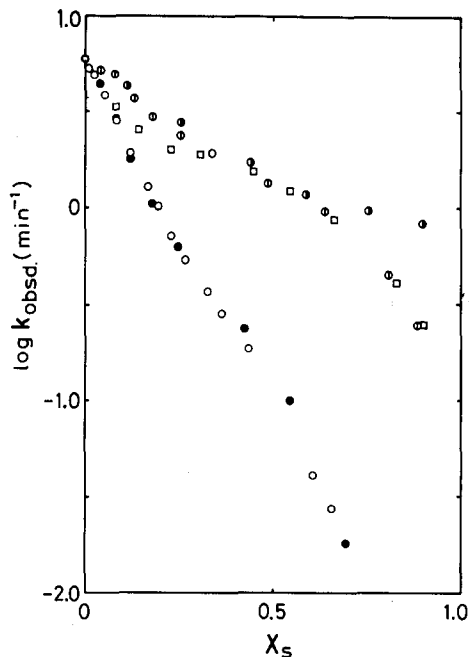


Fig. 2. Keto-enol transformation rate in mixed aqueous solvents, 25°C. Organic component: \bullet , methanol; \circ , ethanol; \square , *t*-butanol; \circ , dioxane; \bullet , acetonitrile.

enol fractions are summarized in Table 1. In every case the enol content increases with increasing the mole fraction of organic solvent. It seems that the enol fraction in pure solvents decreases roughly with increasing the dielectric constant of the medium, but the neat correlation between the enol fractions and the dielectric constants has not been found. The experimentally observed rate constants, k_{obs} , are related by the following relations to the enolization and the ketonization rate constants, k_e and k_k , respectively.

$$k_e = f k_{\text{obs}}$$

$$k_k = (1 - f) k_{\text{obs}}$$

$$f = [\text{enol}] / ([\text{enol}] + [\text{keto}]).$$

In Figs. 3 and 4, the logarithms of the deduced rate constants are plotted vs X_s . The temperature dependence of k_e and k_k are evaluated in dioxane–water and methanol–water systems at the same solvent composition ($X_s = 0.50$). The enol fractions determined by NMR are 0.70, 0.67 and 0.61 in dioxane–water; 0.55, 0.47 and 0.48 in methanol–water for 0, 25 and 39°C, respectively. The relation of k_e and k_k to temperature is resolved by following equations in terms of the transition-state theory[13].

$$\ln \frac{h k_e}{k T} = \frac{\Delta S_e^\ddagger}{R} - \frac{\Delta H_e^\ddagger}{R T}$$

$$\ln \frac{h k_k}{k T} = \frac{\Delta S_k^\ddagger}{R} - \frac{\Delta H_k^\ddagger}{R T}$$

The plots of $\log(k_e/T)$ and $\log(k_k/T)$ vs $1/T$ show good

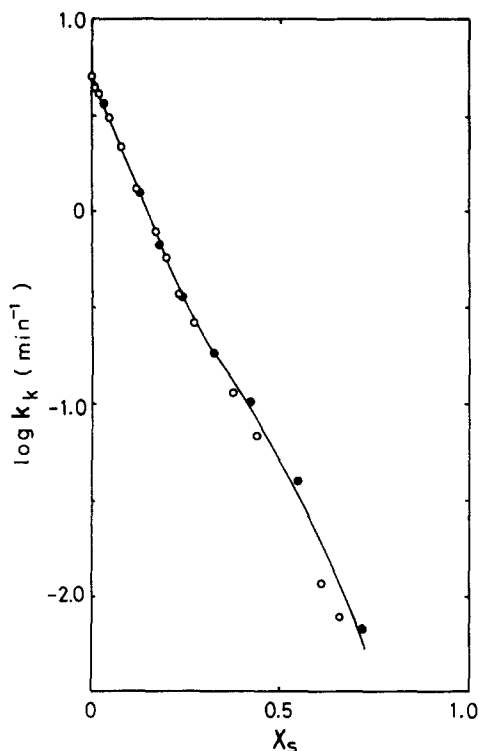


Fig. 3(a). Variation of ketonization rate constant with mole fraction of organic (aprotic) solvents: ○, dioxane; ●, acetonitrile.

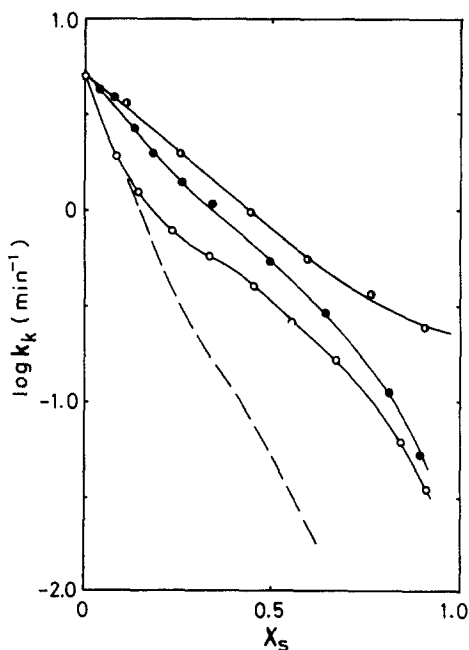


Fig. 3(b). Variation of ketonization rate constant with mole fraction of organic (protic) solvents: ●, methanol; ●, ethanol; ○, *t*-butanol; —, aprotic solvents (cf. Fig. 3a).

linearity as is shown in Fig. 5. According to the usual manner, the activation parameters are estimated for each reaction. The results are summarized in Table 2.

DISCUSSION

Effect of water-aprotic solvent mixtures

As is shown in Fig. 3(a) and 4(a), k_e and k_k decrease monotonously with increase of aprotic content. In spite of the large difference of polarities in two organic solvents, dioxane (dielectric constant 2.209) and acetonitrile (37.5), no essential difference in the reaction rates is observed. From these results, it is clear that the dominant factor governing the ketonization and enolization reactivities in water-aprotic solvents systems is the water content. Probably, this suggests that the transformation may proceed through solvation of water in the transition state. Furthermore, from the plots of $\log k_k$ vs $\log X_w$ (X_w : the molar fraction of water) the participation order of water at highly aqueous region ($X_w > 0.7$) is calculated as 11.5 and 11.3 in dioxane and acetonitrile systems, respectively. In the same manner the participation order for the enolization reaction is estimated as 3.6 and 4.3 in dioxane and acetonitrile systems, respectively.

For the tautomerization mechanism we postulate the ionization mechanism involving the proton transfer through solvent molecules. The simplified scheme may be written as follows like as the representation of Sutin *et al.*[14].

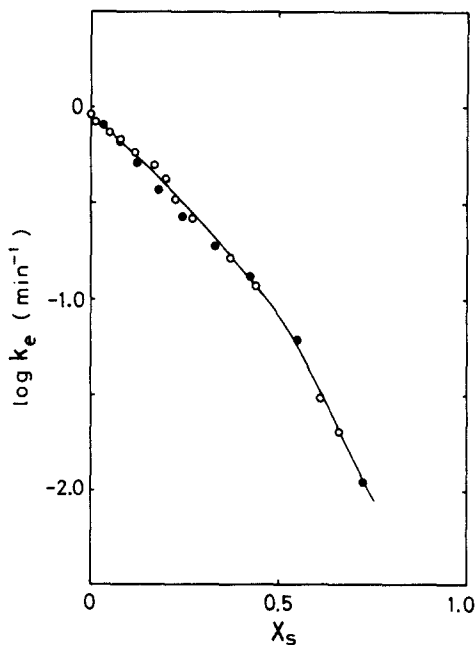
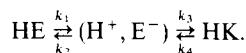


Fig. 4(a). Variation of enolization rate constant with mole fraction of organic (aprotic) solvents: ○, dioxane; ●, acetonitrile.

Table 1. Enol fractions estimated by NMR technique in mixed aqueous solvents, 25°C.
 [acetylacetone] = 0.10 M

Organic component	Methanol		Ethanol		<i>t</i> -Butanol*		Dioxane†		Acetonitrile§	
	X_s	f	X_s	f	X_s	f	X_s	f	X_s	f
	0	0.15								
	0.111	0.19	0.039	0.17	0.079	0.38	0.049	0.20	0.036	0.19
	0.253	0.30	0.081	0.22	0.140	0.49	0.081	0.24	0.078	0.23
	0.441	0.44	0.132	0.28	0.233	0.59	0.119	0.31	0.125	0.29
	0.592	0.53	0.184	0.34	0.313	0.66	0.170	0.39	0.180	0.35
	0.759	0.58	0.256	0.42	0.447	0.74	0.199	0.43	0.246	0.43
	0.904	0.70†	0.336	0.49	0.549	0.79	0.273	0.51	0.327	0.51
	1.0	0.74†	0.489	0.61	0.667	0.82	0.375	0.60	0.425	0.57
			0.640	0.68	0.836	0.85	0.438	0.64	0.550	0.60
			0.812	0.75	0.907	0.86	0.626	0.73	0.723	0.62
			0.891	0.78	1.0	0.87	1.0	0.84	1.0	0.60
			1.0	0.81†						

*Estimated from the apparent molar absorptivity. [acetylacetone] = 1.00×10^{-4} M.

†Quoted value[9].

§At 39°C.

 Table 2. Values of activation parameters corresponding to k_i and k_k

	Dioxane-water ($X_s = 0.50$)		Methanol-water ($X_s = 0.50$)	
	ΔH^\ddagger (kcal. mole ⁻¹)	ΔS^\ddagger (cal. mole ⁻¹ . deg ⁻¹)	ΔH^\ddagger (kcal. mole ⁻¹)	ΔS^\ddagger (cal. mole ⁻¹ . deg ⁻¹)
k_i	9.55 ± 0.35	-40.1 ± 1.1	12.6 ± 0.5	-24.8 ± 1.7
k_k	11.5 ± 0.4	-34.7 ± 1.1	13.8 ± 0.5	-21.0 ± 1.6

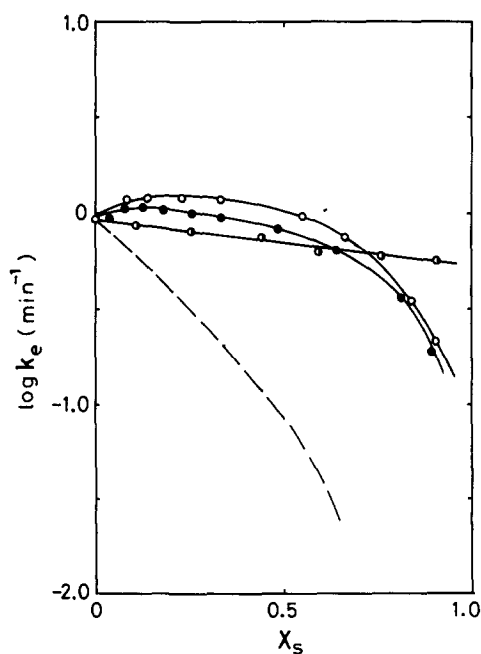


Fig. 4(b). Variation of enolization rate constant with mole fraction of organic (protic) solvents: ●, methanol; ●, ethanol; ○, *t*-butanol; —, aprotic solvents (cf. Fig. 4a).

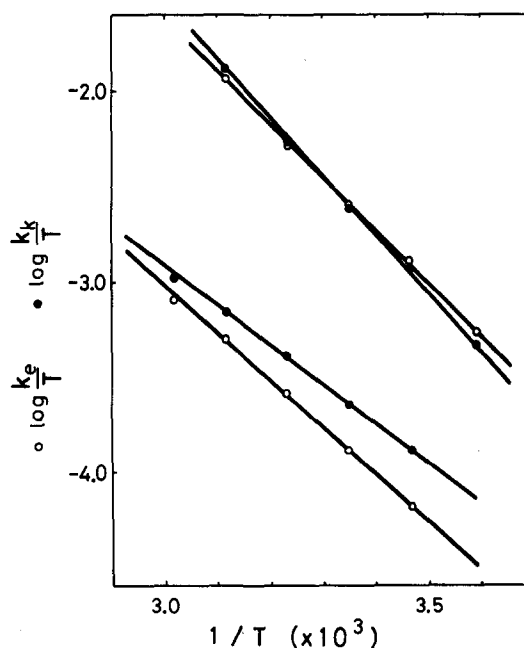


Fig. 5. Temperature dependence on k_e and k_k . Upper lines; methanol-water ($X_s = 0.50$). Lower lines; dioxane-water ($X_s = 0.50$).

In this process, (H^+ , E^-) represents the separately solvated proton and enolate ion or the solvated ion pair as an intermediate. Since the association of enolate ion with proton proceeds very rapidly in highly aqueous media, the observed rate constants should be interpreted by following relations assuming $k_2 \gg k_3$ as in pure aqueous solution[5].

$$k_k = \frac{k_3}{k_2} \cdot k_1$$

$$k_c = k_4.$$

From these relations, the large value of participation order of water for the ketonization reaction, about 11, may be explained by assuming that a breaking of the linkage of intramolecular hydrogen bonding of the enol form of acetylacetone, which is initially not or in poorly solvated state, and a protonation at C-3 of enolate ion are encouraged by the solvation of large number of water molecules at an intermediate transition state. While in the enolization reaction, the smaller orders, 4, may be understood by assuming that the dissociation of the keto form, which may already be hydrated in its initial state[15], does not require so large number of solvated water.

Effect of water-protic solvent mixtures

In Fig. 3(b) a variation of the rate constants of ketonization reaction in water-alcohol mixtures is shown. The effect of alcohol seems to be remarkable compared in the case of the aprotic solvents, and the sequence of this effect is following order; methanol > ethanol > *t*-butanol. In other words, alcohol has a similar role as water in the tautomerization reaction. Considering that the tautomerization reaction is the proton transfer reaction via solvent molecules the preferential effect of hydroxylic solvent must be noticed, and the magnitude of this characteristic effect is necessarily consistent with the acidity strengths of alcohols in the order[16]; methanol > ethanol > *t*-butanol. In the *t*-butanol-water mixtures, the partial depression appears at the region $0.1 < X_s < 0.3$. This phenomena may be explained in terms of the structure formation of water around *t*-butanol in this concentration region[17], indicating a decrease of free water which is available for solvation to the enol form. While for the enolization reaction (Fig. 4b), the rate does not decrease in contrast to the ketonization reaction. Especially in the cases of ethanol and *t*-butanol an increase in X_s causes slightly increase of the rate constant and then decrease gradually. These phenomena can be interpreted by assuming an increase of dynamic basicity of water by hydration to alcohol. The similar observation has been reported for the detritiation of malononitriles[18] and the solvolysis of covalent sulfonylmethyl perchlorates[19].

Otherwise, from the electrostatic viewpoint, a polarity effect of media must be taken into account as another factor governing the reaction. However, a

polarity effect is not necessarily to be considered as the main factor to interpret the present results, that is, when we compared the $\log k_k$'s at a fixed dielectric constant[20], say 70, the following not-consistent values are obtained for each system. The values are as follows.

Organic component	Dioxane	<i>t</i> -Butanol	Ethanol	Methanol
$\log k_k$	0.60	-0.10	-0.30	-0.60

Activation parameters

The activation parameters, the activation enthalpy ΔH^\ddagger and the activation entropy ΔS^\ddagger , are shown in Table 2 at the 95 per cent confidence level. That all ΔS^\ddagger 's show negative values suggests a strong solvation at the polarized transition state (H^+ , E^-). In methanol-water mixture, however, most of the solvent molecules have already associated each other, therefore, the reorientation of water or methanol molecules at transition state may not cause so large variation of ΔS^\ddagger as in aqueous dioxane. The larger negative value for the enolization compared with the ketonization reflects the ordered structure of enol form. As for ΔH^\ddagger , so large variation as ΔS^\ddagger is not observed for two types of mixtures. Consequently, it may be concluded that the rate of tautomerization in mixed aqueous media is primarily governed by the degree of association of solvent molecules.

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