

TAUTOMERIZATION OF ACETYLACETONE AND RELATION OF THE TAUTOMERIZATION CONSTANT TO OTHER EQUILIBRIUM PARAMETERS

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The relative partial pressures of acetylacetonone above mixed aqueous-organic solutions were measured chromatographically and the Gibbs energies of acetylacetonone transfer from water to the mixed solvents were determined and separated into contributions from the keto and enol forms. The tautomerization equilibrium was related to other thermodynamic equilibria and the Gibbs energy of transfer of the keto form was correlated with that of acetone.

Since tautomerization constants generally cannot be described by a simple function of a single physical observable, empirical equations are often used to express the effect of medium on them¹. For acetylacetonone in mixed solvents, however, the conventionally applied functions fail to provide a uniform dependence^{2,3}, and so a different approach to this problem has to be sought. In the present work the tautomerization equilibrium is treated in terms of the Gibbs energy of transfer from water to mixed aqueous-organic solvents.

THEORETICAL

The Gibbs energy of transfer of a weak electrolyte from aqueous solution to a mixed solvent obeys the relation⁴

$$\Delta G_{\text{tr}}^0(\text{electrolyte}) = \Delta G_s^0 - \Delta G_w^0 = 2.3RT(\text{p}K_s - \text{p}K_w), \quad (1)$$

where $\text{p}K$'s are defined conventionally ($\text{p}K = \text{p}H - \log a_{\text{A}^-} + \log a_{\text{HA}}$); the subscripts s and w refer to the mixed and aqueous solutions, respectively. For the undissociated form of a weak electrolyte with a measurable vapour tension, whose concentration in the neutral region can be identified with the total concentration of the substance HA , we can write⁵

$$\Delta G_{\text{tr}}^0(\text{HA}) = RT[\ln (p_r/x)_s - \ln (p_r/x)_w], \quad (2)$$

where x is the mole fraction of solute HA in the solution and $p_r = p'/p_0$ is the ratio of the partial pressure of HA above the solution (p') to that above the pure HA (p_0) (relative partial pressure).

For a saturated solution of solute HA we have similarly⁵

$$\Delta G_{tr}^0(\text{HA}) = RT \ln [(a_{\text{sat}})_w / (a_{\text{sat}})_s]. \quad (3)$$

For a sparingly soluble substance the activity coefficients can be put equal to unity and Eq. (3) can be written in the form

$$\Delta G_{tr}^0(\text{HA}) = RT \ln [(c_{\text{sat}})_w / (c_{\text{sat}})_s]. \quad (4)$$

If the solute exists in a tautomeric equilibrium, the latter can be characterized⁶ by Eq. (5) regarding the enol form as the starting substance and the keto form as the reaction product:

$$K_t = a_{\text{keto}} / a_{\text{enol}} = K_{\text{enol}} / K_{\text{keto}}, \quad (5)$$

where K_{enol} and K_{keto} are the dissociation constants of the respective tautomeric forms.

In the case of tautomerization of a solute, its Gibbs energy of transfer in Eqs (2) and (4) includes not only the transfer of the two isomers in the initial ratio from water to the mixed solvent but also the change in the tautomerization equilibrium:

$$\Delta G_{tr}^0(\text{HA}) = \Delta(G_{tr}^0)_0 + \Delta G_{\text{taut}}, \quad (6)$$

where the first right-hand term refers to the condition $\partial(\text{keto/enol})/\partial S = 0$; since this term includes contributions from the two tautomeric forms, it is convenient to separate it into the two parts. This can be achieved as follows. In terms of the fraction of the solute present in the keto form α , the concentrations of the two tautomeric forms can be written as

$$c_{\text{keto}} = \alpha c_T \quad (7)$$

$$c_{\text{enol}} = (1 - \alpha) c_T, \quad (8)$$

where c_T is the total concentration of the solute. The first right-hand term in Eq. (6) then can be written as

$$\Delta(G_{tr}^0)_0 = \alpha \Delta G_{tr}^0(\text{keto}) + (1 - \alpha) \Delta G_{tr}^0(\text{enol}), \quad (9)$$

where $\Delta G_{tr}^0(\text{keto})$ and $\Delta G_{tr}^0(\text{enol})$ are the Gibbs energies of transfer of the respective tautomeric forms from water to the mixed solvent.

The term ΔG_{taut} in Eq. (6) is the Gibbs energy change in the mixed solvent associated with the change in the activities of the two tautomeric forms when passing from water to this solvent. The activities are interrelated by

$$(a_{\text{keto}})_{\text{w}} + (a_{\text{enol}})_{\text{w}} = (a_{\text{keto}})_{\text{s}} + (a_{\text{enol}})_{\text{s}}. \quad (10)$$

The left-hand and right-hand standard chemical potentials of the keto form in Eq. (10) are identical, and so are those of the enol form (regarding the pure substance, *i.e.* the keto or enol form, as the standard state). Then we have

$$\Delta G_{\text{taut}} = RT \ln [(a_{\text{keto}} a_{\text{enol}})_{\text{s}} / (a_{\text{keto}} a_{\text{enol}})_{\text{w}}]. \quad (11)$$

The activity of the undissociated fraction of the keto or enol form can be substituted by the corresponding concentration (the activity coefficient of a nonelectrolyte can be usually approximated by unity up to a concentration of about 0.1 mol l^{-1}). Combining Eqs (5), (7), and (8) we obtain

$$\alpha = K_{\text{t}} / (1 + K_{\text{t}}), \quad (12)$$

and by substituting Eq. (5) into Eq. (11) we have

$$\Delta G_{\text{taut}} = RT \ln [(K_{\text{t}} a_{\text{enol}}^2)_{\text{s}} / (K_{\text{t}} a_{\text{enol}}^2)_{\text{w}}]. \quad (13)$$

Expressing the activity of the enol form in terms of the fraction α we obtain

$$\Delta G_{\text{taut}} = RT \ln \{ [K_{\text{t}} / (1 + K_{\text{t}})]_{\text{s}} / [K_{\text{t}} / (1 + K_{\text{t}})]_{\text{w}} \}. \quad (14)$$

Thus the Gibbs energy of transfer of solute HA can be calculated by inserting experimental data in Eqs (2) or (4), and the Gibbs energy of tautomerization can be calculated from Eq. (14). Inserted in Eq. (6), the two values enable us to calculate the term $\Delta(G_{\text{tr}}^0)_{\text{o}}$, which is given by the sum of contributions from the two forms according to Eq. (9). One more algebraic equation is necessary for the calculation of the Gibbs energies of transfer of the individual tautomeric forms. This can be found by the following route. If the tautomeric equilibrium in the two systems (water, mixed solvent) has established, the equations

$$(\mu_{\text{keto}}^0)_{\text{w}} - (\mu_{\text{enol}}^0)_{\text{w}} + RT \ln (a_{\text{keto}} / a_{\text{enol}})_{\text{w}} = 0 \quad (15)$$

$$(\mu_{\text{keto}}^0)_{\text{s}} - (\mu_{\text{enol}}^0)_{\text{s}} + RT \ln (a_{\text{keto}} / a_{\text{enol}})_{\text{s}} = 0 \quad (16)$$

hold true. Subtracting them and including Eq. (5) we obtain

$$\Delta G_{tr}^0(\text{enol}) = \Delta G_{tr}^0(\text{keto}) + 2.3RT[(pK_t)_w - (pK_t)_s], \quad (17)$$

where $\Delta G_{tr}^0(\text{keto})$ is given by the difference $(\mu_{\text{keto}}^0)_s - (\mu_{\text{keto}}^0)_w$, and similarly for the enol form. In this manner the missing equation is known and the $\Delta G_{tr}^0(\text{keto})$ and $\Delta G_{tr}^0(\text{enol})$ values can be readily calculated.

EXPERIMENTAL

Acetyl acetone of reagent grade purity (Reakhim, U.S.S.R.) was distilled twice and the fraction boiling at 194°C was collected. Methanol, 2-propanol, dimethyl sulphoxide, dioxane, ethylene glycol, and acetone were commercial chemicals of reagent grade purity (Lachema, Brno), used as received. The organic solvents were mixed with water to obtain binary solvents, defined by the mass fraction (%) of the organic component. The measurements were carried out with solutions prepared by adding 0.5 ml of acetylacetone or acetone to 5 ml of these binary solvents. The mole fractions of the solutes were calculated by means of density data of the mixed solvents and the solute⁷⁻¹².

The temperature dependence of the tautomerization constant of acetylacetone was obtained from spectral measurements in the UV region, performed with the use of a Pye-Unicam SP 8-100 instrument in 1 cm quartz cells; the requisite absorptivity data were taken from ref.².

The chromatographic analyses of the equilibrium vapours above the solutions were carried out on a Chrom 4 gas chromatograph fitted with a flame ionization detector (Laboratorní přístroje, Prague). The column was stainless steel 3 m × 4 mm, packed with Chromaton N-AW-DMCS (0.10–0.125 mm) with 10% OV-210; injection temperature 200°C, column temperature 130°C, detector temperature 150°C, nitrogen, hydrogen, and air flow rates 18.8, 30, and 450 ml . min⁻¹, respectively. The samples were thermostatted in 30 ml glass vessels for 60 min. One ml volumes of the equilibrium vapours were injected by using a 1 ml glass syringe (Chirana, Stará Turá).

RESULTS AND DISCUSSION

Application of the treatment given in the Theoretical is demonstrated on the equilibria of acetylacetone. Its relative partial pressures at $(25 \pm 0.1)^\circ\text{C}$ were measured chromatographically with an accuracy of 2% and the data were inserted in Eq. (2) to calculate the ΔG_{tr}^0 values of acetylacetone. The ΔG_{taut} values were then calculated from Eq. (14) using the K_t data from ref.². These results were employed to calculate the $\Delta G_{tr}^0(\text{keto})$ and $\Delta G_{tr}^0(\text{enol})$ values by means of Eqs (6) and (17). The relative partial pressures and the Gibbs energies of transfer of acetylacetone and its tautomeric forms are given in Table I.

The above relations allow also the Gibbs energy of transfer of the acetylacetone ion from water to the mixed solvent to be calculated. Expressing the dissociation constant of acetylacetone (HA) as

$$K = a_{\text{H}^+} a_{\text{A}^-} / a_{\text{HA}}, \quad (18)$$

TABLE I

Relative partial pressures of acetylacetone above solvents and the Gibbs energies of transfer from water to mixed solvents for acetylacetone, its keto and enol forms and its anion

w^a %	p_r	$\Delta G_{tr}^0(\text{HA})$ kJ mol ⁻¹	$\Delta G_{tr}^0(\text{keto})$ kJ mol ⁻¹	$\Delta G_{tr}^0(\text{enol})$ kJ mol ⁻¹	$\Delta G_{tr}^0(\text{A}^-)$ kJ mol ⁻¹
water-methanol					
20	0.536	-2.07	-2.80	-4.93	0.72
40	0.465	-2.75	-3.54	-6.50	1.69
60	0.370	-3.47	-3.61	-7.92	2.19
80	0.317	-4.53	-3.36	-8.97	5.56
90	0.247	-5.39	-3.81	-9.69	7.25
water-2-propanol					
20	0.414	-2.86	-3.71	-6.05	4.57
50	0.203	-4.81	-4.19	-9.31	21.26
70	0.163	-6.07	-3.91	-10.21	—
90	0.169	-6.85	-1.90	-9.83	—
water-1,4-dioxane					
10	0.509	-1.43	-1.93	-2.87	2.30
20	0.479	-1.77	-2.56	-4.38	5.43
30	0.343	-2.82	-3.66	-6.29	7.60
40	0.279	-3.59	-4.24	-7.66	9.87
50	0.242	-4.76	-5.08	-9.13	11.0
70	0.122	-7.20	-6.39	-11.68	—
90	0.073	-9.51	-6.75	-13.43	—
water-ethylene glycol					
10	0.592	-1.21	-1.85	-3.12	—
30	0.707	-1.11	-1.96	-4.37	—
50	0.691	-1.59	-2.04	-5.88	—
70	0.704	-2.09	-0.96	-6.56	—
90	0.605	-3.22	-0.99	-7.33	—
water-dimethyl sulphoxide					
20	0.521	-2.06	0.0	0.0	—
40	0.597	-2.14	-2.98	-5.51	—
60	0.530	-2.97	-3.67	-6.94	—
80	0.294	-5.21	-5.48	-9.60	—

^a Mass fraction of organic constituent in mixed solvent.

rearrangement of Eq. (1) gives^{13,14}

$$2.3RT(\text{p}K_s - \text{p}K_w) = \Delta G_{\text{tr}}^0(\text{H}^+) + \Delta G_{\text{tr}}^0(\text{A}^-) - \Delta G_{\text{tr}}^0(\text{HA}). \quad (19)$$

The dissociation constants $\text{p}K_s$ and $\text{p}K_w$ are available², the $\Delta G_{\text{tr}}^0(\text{HA})$ values are as given in Table I, the Gibbs energies of transfer of the H^+ ion can be found in refs¹⁵⁻¹⁷, and so $\Delta G_{\text{tr}}^0(\text{A}^-)$ is the only unknown left in Eq. (19). Conversion of the Gibbs energies of transfer of the H^+ ion to the mole fraction scale was accomplished by means of the equations in ref.¹⁷ and the known densities⁷⁻¹¹. The data in Table I allow the effect of medium on the dissociation and tautomerization of acetylacetone to be discussed. This table shows that the transfer of one mole of the anion from water to the mixed solvent is accompanied by an increase in the Gibbs energy. On this transfer, both the keto and enol forms of acetylacetone become weaker acids². This is so because the transfer of acetylacetone from water to the mixed solvent is associated with a reaction during which the Gibbs energy of the system decreases. Table I demonstrates that this reaction is such that the amount of anions decreases and that of neutral molecules increases, which explains the decrease in acidity of both forms. Moreover, the transfer of enol form from water into the mixed solvent is accompanied by greater decrease of Gibbs energy than the transfer of keto form and this leads to a decrease in the tautomerization constant value in Eq. (5), as has been actually observed^{2,3}. It can be concluded that the changes in the tautomerization and dissociation equilibria arise from changes in the Gibbs energy of transfer of the various species, associated, among others, with changes in their solvation. In this respect our previous qualitative considerations² are specified in a more detailed manner.

For gaining a better insight into the tautomerization effects, the temperature dependence of the tautomerization constant of acetylacetone in water was examined spectroscopically. The values of $K_t = 7.13, 8.21, \text{ and } 9.24$ were measured at 298.1, 308.6, and 318.0 K, respectively. The reaction heat of conversion of the enol to the ketone, calculated from the van't Hoff isobar, is $\Delta H^0 = 10.0 \text{ kJ mol}^{-1}$ at 298.1 K, and the entropy term, obtained from the definition relation $\Delta G^0 = \Delta H^0 - T\Delta S^0$, is $\Delta S^0 = 49.9 \text{ J K}^{-1} \text{ mol}^{-1}$ at this temperature. The isomerization of the enol to the ketone is seen to be endothermic. This can be well understood with regard to the fact that in addition to changes in the resonance and solvation energies, the reaction is associated with a breakdown of the stable hydrogen bond between the OH group of the enol and its carbonyl oxygen atom^{18,19}. The positive value of the entropy term is not surprising either, because the reaction proceeds from the planar enol form toward the freely rotating ketone, hence, toward a state of higher disorder.

Equations have been suggested^{20,21} for describing the interdependences of the Gibbs energies of transfer of chemically related substances. For extending the experimental data base, the Gibbs energies of transfer of acetone from water to the

TABLE II

Relative partial pressures of acetone and its Gibbs energies of transfer from water to mixed solvents

w^a %	P_r	ΔG_{tr}^0 kJ mol^{-1}	w^a %	P_r	ΔG_{tr}^0 kJ mol^{-1}
water-methanol			water-ethylene glycol		
20	0.302	0.45	10	0.304	-0.96
40	0.246	-0.38	30	0.339	-1.03
60	0.221	-0.80	50	0.348	-1.39
80	0.205	-1.65	70	0.369	-1.78
90	0.214	-1.79	90	0.389	-2.39
water-2-propanol			water-dimethyl sulphoxide		
20	0.248	-0.18	20	0.329	-0.95
50	0.211	-2.98	40	0.374	-1.04
70	0.225	-3.53	60	0.413	-1.34
90	0.253	-4.11	80	0.391	-2.23
water-1,4-dioxane					
10	0.275	-1.14	50	0.201	-2.88
20	0.252	-1.56	70	0.208	-3.51
30	0.247	-1.83	90	0.209	-4.55
40	0.246	-2.09	—	—	—

^a Mass fraction of organic constituent in mixed solvent.

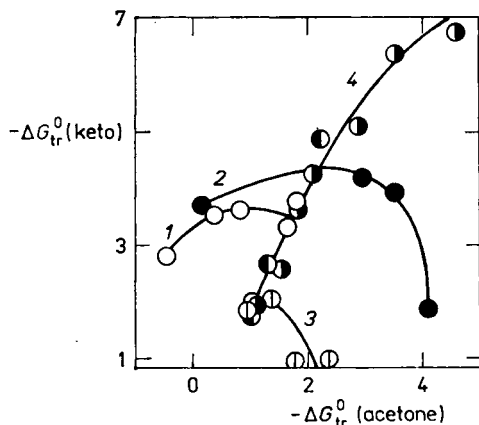


FIG. 1

Interdependence of the Gibbs energies of transfer from water to mixed solvent for the keto form of acetylacetone and acetone. System: 1 water-methanol (○), 2 water-2-propanol (●), 3 water-ethylene glycol (○), 4 water-1,4-dioxane (●), and water-dimethyl sulphoxide (●)

mixed solvents were also measured; Eq. (2) was used for determining the ΔG_{tr}^0 value for this solute. The relative partial pressures and the Gibbs energies of transfer are given in Table II. The interdependence between the ΔG_{tr}^0 values of the keto form of acetylacetone and acetone is shown in Fig. 1. The solute concentrations are rather high for this interrelation and cannot be substituted for the activities. This can be responsible for the fact that the extrapolated curves do not pass through the origin of the coordinate system. Still, the observed dependences can be divided into two groups, one including the individual dependences for the water-alcohol systems, the other including the dependences for the water-dimethyl sulphoxide and water-1,4-dioxane systems which can be fitted by a single curve within the limits of experimental error. The variability of the interdependences of the ΔG_{tr}^0 values for the first group of solvents is too high to enable a unique conclusion to be drawn. In the second group, it is noteworthy that dioxane disturbs the structure of water at lower concentrations than dimethyl sulphoxide²². This fact is consistent with the shape of curve 4 in Fig. 1, whose upper part is determined by the points for the water-dioxane system solely. This suggests that the Gibbs energy of transfer of substances (species) may be affected not only by their solvation but also by changes in the structure of water and/or the organic component²³.

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