

PROTOLYTIC DISTRIBUTION AND SOME OTHER EQUILIBRIA OF C₇ β-DIKETONES

F. VLÁČIL, BASSAM M. SAYEH* and J. KOUCKÝ**

*Department of Analytical Chemistry,
Institute of Chemical Technology, 166 28 Prague 6*

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Protolytic, distribution and tautomeric (keto-enol) equilibria were studied with compounds: 2,4-heptanedione, 3,5-heptanedione, 3-methyl-2,4-hexanedione and 5-methyl-2,4-hexanedione. The dissociation constants of these diketones and of their enol-forms, the distribution constants in water-chloroform and water-benzene systems (*I* 0.1) and the solubilities of the diketones in water at 25°C have been determined. The IR and NMR spectra of the β-diketones were measured and the content of their enols in the pure substances and in aqueous solutions was determined. A method for their spectrophotometric determination in aqueous solutions has been developed. On the basis of the results obtained, 5-methyl-2,4-hexanedione has been selected as a reagent for extraction of metal chelates.

A method for separation of inorganic substances which has recently undergone rapid development is reversed-phase partition chromatography (RPPC). It is also called extraction chromatography, since an extractant forms the stationary phase. Both reagent solutions forming ion-associates (*e.g.* high-molecular amines) and some chelating agents have been used as stationary phases^{1,2}. The RPPC of inorganic compounds has primarily been studied for separations on the radiochemical scale. The amount of a compound that can theoretically be deposited in the bed can be characterized by the overall extraction capacity of the bed, analogous *e.g.* to the exchange capacity of an ion exchange column, equal to the amount of substance of extractant deposited on the support in the bed. A small extraction bed capacity (*e.g.* ≈ 1 μmol/g support³) suffices for radiochemical separations. For separations in analytical chemistry, such a low extraction capacity would be sufficient if a suitable detection method were available and the ions to be separated were present at concentrations of the same order. However, if a sensitive detection technique is not known or if separations are to be performed in trace analysis, where the ratio of separated components is large, column chromatography must be used and the extraction capacity of the column must be substantially larger than in separations on radiochemical, carrier-free scale.

For these purposes it is preferable when the extractant is a liquid, since, with a certain sorption capacity of the support, the maximum extraction capacity of the column can be attained. Liquid extractants also enable the column capacity ratio to be changed in a wide interval. RPPC extractants need not be selective.

The above requirements placed on extractants are met by aliphatic β-diketones; acetylacetone, commonly used for extractions, cannot be used in RPPC, because of its considerable solubility in

Present addresses: * Scientific Studies and Research Centre, Damascus, Syrian Arab Republic, ** Preciosa, Jablonec n. N.

water. This inconvenient property can be eliminated either by substitution with a halogen or by lengthening the β -diketone chain. We decided to utilize the latter method and looked for an aliphatic β -diketone with an acceptably low solubility in water, having as short a chain as possible. The acidity of the β -diketone enol-forms decreases with increasing chain length and for extraction of readily hydrolyzable ions reagents with higher dissociation constants are more suitable. These requirements are met by C_7 β -diketones, *i.e.* 2,4-heptanedione (*I*), 3,5-heptanedione (*II*), 3-methyl-2,4-hexanedione (*III*) and 5-methyl-2,4-hexanedione (*IV*). Among other possible C_7 isomers, 3-ethyl-2,4-pentanedione, whose properties will be very close to *III*, and 3,3-dimethyl-2,4-pentanedione, which cannot enolize, were not considered.

Among the reagents studied, the extraction of nine metal chelates by the solution of reagent *II* in benzene⁴ and synergistic extraction of zinc with the same reagent⁵ have already been studied. Protolytic equilibria have been studied with *IV* (refs⁶⁻⁸), *I* (ref.⁷) and *II* (ref.⁹).

Since the extraction properties of these derivatives have not been generally studied and some constants which are required when these substances are used as stationary phases in RPPC, have not been determined, we directed the present work to determination of the solubility of these derivatives in water, of their distribution and dissociation constants and to study of the keto-enol equilibrium. The aim of this work was to choose from the studied substances the best reagent for the extraction of metal ions from aqueous solutions.

EXPERIMENTAL

Preparation of the Reagents

The β -diketones were prepared by the Claisen condensation, using sodium hydride¹⁰ (Lachema, Brno). The esters required were dried with sodium hydride (butyrate and isobutyrate) or with anhydrous potassium carbonate (acetate and propionate) and were distilled before use. Acetone,

TABLE I

Light Absorption Maxima and the Molar Absorption Coefficients of the β -Diketone in Various Media

| β -Diketone | Water | | | 0.05M-HClO ₄ | | | 0.05M-NaOH | | |
|-------------------|---|------------------------|---|---|------------------------|---|---|------------------------|---|
| | $c \cdot 10^4$ mol · l ⁻¹ | λ_{\max} nm | ϵ_{\max} mol ⁻¹ · l · cm ⁻¹ | $c \cdot 10^4$ mol · l ⁻¹ | λ_{\max} nm | ϵ_{\max} mol ⁻¹ · l · cm ⁻¹ | $c \cdot 10^5$ mol · l ⁻¹ | λ_{\max} nm | ϵ_{\max} mol ⁻¹ · l · cm ⁻¹ |
| <i>I</i> | 1.360 | 275 | 1 930 | 1.360 | 275 | 1 880 | 5.412 | 294 | 8 320 ± 310 |
| <i>II</i> | 3.031 | 255 | 1 080 | 3.031 | 255 | 1 020 | 3.789 | 294 | 18 190 ± 260 |
| <i>III</i> | 17.343 | 288 | 220 | 17.343 | 288 | 183 ± 13 | 10.440 | 307 | — ^a |
| <i>IV</i> | 0.6322 | 275 | 2 310 | 0.6322 | 275 | 2 260 | 1.522 | 294 | 18 130 ± 570 |

^a Decomposition.

methyl ethyl ketone and diethyl ketone were dried with anhydrous cupric sulphate and distilled. The β-diketones were extracted into ether from the acidified reaction mixture, ether was distilled off, and the β-diketones were fractionated under vacuum. The yields of the diketones (in per cent of theoretical) and the distillation conditions had the following values: *I* 43%, 75–78°C/18 Torr; *II* 36%, 75°C/33 Torr; *III* 36%, 62°C/25 Torr; *IV* 39%, 59–60°C/18 Torr.

About 10% of impurities were detected in the diketones by gas-liquid chromatography. The diketones were purified by separating the cupric salts employing a modified procedure¹¹ and recrystallizing from methanol. After washing with water, methanol and ether and drying, blue to green needles are formed, with the melting points (Koffler): *I* 164.5°C; *II* 210°C; *III* 175°C (decomposition); *IV* 172°C, which are in agreement with the literature data¹². The β-diketones were liberated from the cupric salts and the pure substances were obtained by column distillation; the boiling point values are: *I* 60.5–62.5°C/15 Torr; *II* 63–65°C/18 Torr; *III* 70–71°C/14 Torr; *IV* 53°C/9 Torr. The yield was 20–25% of the preparation before the purification. The GLC showed that all diketones were chemically pure, except *I*. Diketone *I* still contained about 10% impurities; it was obtained chemically pure by preparative GLC. For C₇H₁₂O₂ (128.2) calculated: 65.59% C, 9.44% H, found: *I* 65.63% C, 9.60% H; *II* 66.12% C, 9.55% H; *III* 64.61% C, 9.52% H; *IV* 65.81% C, 9.53% H.

Chemicals and Instruments

All the chemicals employed were of *p.a.* purity. Deionized water was used and was distilled in a glass apparatus for light absorption measurements; for potentiometric measurements this water was freed of carbon dioxide by boiling. Chloroform *p.a.* was shaken with a 5% solution of sodium carbonate and washed with water until the reaction of the water was neutral. Benzene was saturated with water at 25°C. A standard perchloric acid solution was standardized with recrystallized thallium(I) carbonate and by the iodide-iodate method. The titre of a carbonate-free sodium hydroxide standard solution was determined by potentiometric titration with a perchloric acid standard solution.

Potentiometric titrations were performed on an E 436 potentiograph (Metrohm, Herisau, Switzerland) with a 109 UX glass electrode and an s.c.e., saturated with sodium chloride. The pH was measured with a PHK 1 instrument (Mikrotechna, Prague) and an SEAJ combined electrode (Laboratorní přístroje, Prague). If not stated otherwise, the measuring cells were calibrated using a series of NBS standard buffers¹³. Spectrophotometric measurements were carried out on VSU 2 and Specord UV-VIS instruments (both C. Zeiss, Jena) and on an SF 4 spectrophotometer (USSR). The measuring potentiometers of the instruments were calibrated using a solution of 0.0400 g K₂CrO₄ in one litre of 0.05M-KOH (ref.¹⁴) and the wavelength scale was calibrated with selected lines of a mercury lamp¹⁵.

RESULTS

The Solubility of the β-Diketones in Water

The solubility of the β-diketones in water was determined by potentiometric titration with a sodium hydroxide standard solution; in this manner the diketone concentration was determined in a saturated aqueous solution at 25 ± 0.1°C, obtained after 12 hours standing of a mixture of a diketone with water in a thermostat, with occasional stirring. The solubility of the individual diketones (mol l⁻¹) is given as the average of

two measurements: *I* 0.103, *II* 0.112, *IV* 0.0978. The solubility of *III* could not be determined, since the substance decomposed on prolonged contact with water.

UV, IR and NMR Spectra

Diketone solutions in water were prepared with the concentration given in Table I. Their absorption spectra were measured in the range, 240–340 nm. Further, changes in the shapes of the spectra with varying concentrations of perchloric acid or sodium hydroxide were followed. It was found that the shape of the spectrum and the absorbance at the maximum do not change at concentrations above 0.01M-HClO₄ or 0.05M-NaOH. Further, variations in the absorbance with time were followed at the λ_{\max} of the non-dissociated form of the aqueous solutions of the diketones and of their solutions in 0.05M-HClO₄ and 0.05M-NaOH. The results are given in Table II. The

TABLE II

The Time Dependence of the Absorbance of the β -Diketone Solutions at λ_{\max} ^a
c (diketone *I, II, IV*) 10⁻⁴M, *c* (diketone *III*) 10⁻³M, *t* 25°C; a 1 cm cuvette was employed.

| Medium | Time | | | | |
|-------------------|--------|--------|-------|-------|-------|
| | 15 min | 30 min | 1 h | 24 h | 7 d |
| <i>I</i> | | | | | |
| Water | 0.397 | 0.383 | 0.378 | 0.372 | 0.357 |
| Acid ^b | 0.392 | 0.392 | 0.382 | 0.380 | 0.395 |
| Base ^c | 0.356 | 0.356 | 0.353 | 0.266 | 0.082 |
| <i>II</i> | | | | | |
| Water | 0.147 | 0.152 | 0.152 | 0.157 | 0.150 |
| Acid | 0.139 | 0.140 | 0.141 | 0.156 | 0.159 |
| Base | 0.667 | 0.653 | 0.649 | 0.477 | 0.077 |
| <i>III</i> | | | | | |
| Water | 0.505 | 0.499 | 0.497 | 0.433 | — |
| Acid | 0.439 | 0.436 | 0.432 | 0.430 | — |
| Base | 0.913 | 0.296 | 0.200 | 0.115 | — |
| <i>IV</i> | | | | | |
| Water | 0.673 | 0.673 | 0.670 | 0.687 | 0.687 |
| Acid | 0.662 | 0.662 | 0.658 | 0.687 | 0.670 |
| Base | 0.749 | 0.749 | 0.738 | 0.666 | 0.422 |

^a λ_{\max} values for the diketones (the HL form) are given in Table I; ^b 0.05M-HClO₄; ^c 0.05M-NaOH.

wavelengths of the absorption maxima (λ_{\max}) obtained for the diketones are summarized in Table I, together with their molar absorption coefficients at λ_{\max} , calculated from the given diketone concentration. The absorption coefficients of the anions L⁻ of the diketones *I*, *II* and *IV* and of the non-dissociated form (HL) of *III* were calculated from the linear portion of the calibration dependence, $A = f(c)$ and are given for 95% confidence limits, calculated from the standard deviation of the slope of a regression line obtained from n points using the Student distribution for $n-2$ degrees of freedom.

The IR spectra of the β-diketones alone and of their solutions in tetrachloromethane were measured from 600 to 4000 cm⁻¹ on a Perkin-Elmer 325 instrument. The following absorption bands were found for the pure diketones:

I 894 (m), 966 (w), 1260 (m), 1450 (m), 1470 (m), 1606 (vs), 1700 (w), 2868 (m), 2928 (m), 3080 (m) cm⁻¹.

II 812 (w), 855 (w), 945 (w), 975 (w), 1062 (m), 1145 (w), 1200 (m), 1312 (m), 1350 (m), 1375 (m), 1412 (m), 1462 (s), 1620 (vs), 1705 (s), 2930 (m), 2980 (s) cm⁻¹.

III 967 (w), 1030 (w), 1150 (m), 1188 (m), 1232 (w), 1358 (m), 1408 (w), 1460 (m), 1600 (w), 1705 (vs), 2930 (w) 2995 (m) 3180 (w) cm⁻¹.

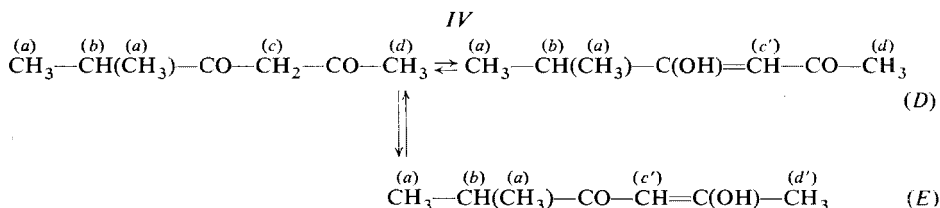
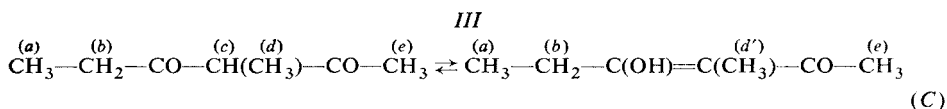
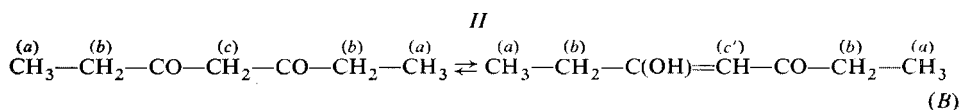
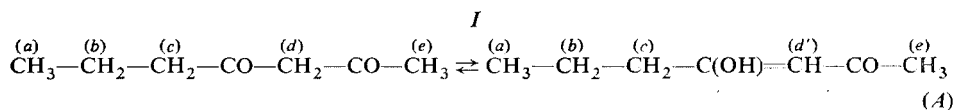
IV 837 (w), 915 (s), 955 (m), 1025 (w), 1082 (m), 1138 (s), 1175 (w), 1220 (s), 1245 (s), 1325 (s), 1365 (s), 1388 (s), 1417 (s), 1450 (s), 1605 (vs), 1705 (m), 2880 (m), 2930 (m), 2990 (vs) cm⁻¹.

From the ratio of the band intensities at 1600 cm⁻¹ and 1700 cm⁻¹, the approximate contents of the enol-form were calculated for *II* and *IV*; for the pure substances it amounted to 76 and 85%, respectively.

TABLE III
Chemical Shifts (δ) of the β-Diketones
Varian XL-100-15, 100 MHz, 37°C, tetramethylsilane internal standard.

| β-Diketone | Functional group | | | | | |
|------------|------------------|------|------|------|------|------|
| | a | b | c | d | e | d' |
| <i>I</i> | 0.97 | 1.65 | 2.25 | 3.57 | 2.10 | 5.50 |
| <i>II</i> | 1.07 | 2.30 | 3.52 | 5.50 | | |
| <i>III</i> | 1.00 | 2.60 | 3.82 | 1.26 | 2.20 | 1.50 |
| <i>IV</i> | 1.10 | 2.44 | 3.60 | 2.16 | 5.54 | 2.00 |

The NMR spectra of the purified β -diketones were obtained on BS 477 (60 MHz; Tesla, Brno) and Varian XL-100-15 (100 MHz; Palo Alto, USA) instruments, using tetramethylsilane as an internal standard. The characteristic chemical shifts (δ) (Table III) were obtained for individual functional groups in diketones *I–IV*, denoted in the schemes:



From the integrated intensities of the singlets corresponding to protons in the $\text{—CH}_2\text{—}$ (*K*) and —CH= (*E*) groups, the contents of the enol-form in the individual diketones (*P*, %) were calculated using the relation¹⁶: $P = 200E/(2E + K)$, obtaining *P*(%): *I* 91 (measured in CDCl_3), *II* 82, *III* 70, *IV* 91 (or 88 in CDCl_3). Virtually the same enol content in *IV* (92%) was calculated from the integrals of the peaks corresponding to the protons of the terminal methyl group, using the relation, $P = 100E/(E + K)$ (ref.¹⁷).

Dissociation Constants

Fresh aqueous solutions of diketones *I–IV* were prepared at concentrations of 0.0112M — *I*, 0.01445M — *II*, 0.0330M — *III* and 0.0153M — *IV* and 25 ml (*I*, *IV*) or 20 ml (*II*, *III*) of these solutions were titrated with 0.1M-NaOH at 25°C, using the potentiograph. From the measured voltage values and using a calibration graph, the

pH values corresponding to the H⁺ activity were determined and the mixed dissociation constants, $(K_a)_m$, were calculated from the relationship valid for pH > 9:

$$(pK_a)_m = \text{pH} + \log [(c_{\text{HL}} + [\text{OH}^-]) / (c_{\text{L}^-} - [\text{OH}^-])]. \quad (1)$$

The $(pK_a)_m$ values were recalculated to the thermodynamical values, $(pK_a)_T$. Average K_a values and the appropriate confidence limits were calculated (using the range and the tabulated coefficient¹⁸), the average was converted to the pK_a value and is given with confidence limits corresponding to the larger of the two possible values (Table IV).

The dissociation constant of *IV* was also determined spectrophotometrically (λ 294 nm), obtaining a value of 9.47 ± 0.02 from the calculation according to Eistert and Reiss¹⁹ or 9.42 by a graphical method²⁰.

TABLE IV
The $(pK_a)_T$ Values of the β-Diketones at 25°C

| β-Diketone | $(pK_a)_T$ | n^a | R^b |
|------------|------------------|-------|-----------------------|
| <i>I</i> | 9.34 ± 0.01 | 10 | $0.47 \cdot 10^{-10}$ |
| <i>II</i> | 10.04 ± 0.01 | 8 | $0.62 \cdot 10^{-11}$ |
| <i>III</i> | 11.20 ± 0.03 | 8 | $1.11 \cdot 10^{-12}$ |
| <i>IV</i> | 9.43 ± 0.01 | 10 | $0.26 \cdot 10^{-10}$ |

^a The number of measured pH values from which pK_a was calculated. ^b Range of the K_a values in the series used for the calculation of the given $(pK_a)_T$ value

Distribution Constants

Solutions of diketones *I–IV* in chloroform or benzene were shaken with equal volumes of a 0.1M-NaClO₄ aqueous solution at 25°C until equilibrium was established. The diketone concentration was determined spectrophotometrically in aliquots of the aqueous phases, using the ϵ_{max} values given in Table I. Diketones *I*, *II* and *IV* were determined in a medium of 0.05M-NaOH, *III* in a medium of 0.05M-HClO₄. The validity of the Lambert–Beer law was verified up to the concentrations: *I* $9.7 \cdot 10^{-5}$ M, *II* $4.6 \cdot 10^{-5}$ M, *III* $5.3 \cdot 10^{-4}$ M, *IV* $9.0 \cdot 10^{-5}$ M. The distribution constants were determined at various initial diketone concentrations in the organic solvents. The results obtained are given in Table V.

The K_D values for the diketones were determined by two-phase potentiometric titration²¹ in both the above systems. A solution of enolate L⁻ was titrated using

TABLE V

The Distribution Constants (K_D) of the β -Diketones in Systems of Water (0.1M-NaClO₄) and Benzene or Chloroform

| β -Diketone | Water-benzene | | Water-chloroform | |
|-------------------|--------------------------|-------|--------------------------|-------|
| | c_{org} , mol/l | K_D | c_{org} , mol/l | K_D |
| <i>I</i> | 0.6482 | 82.1 | 0.6482 | 304 |
| | 0.0929 | 80.7 | 0.0703 | 290 |
| | 0.00929 | 81.3 | 0.00703 | 289 |
| <i>II</i> | 0.7092 | 53.2 | 0.7184 | 174 |
| | 0.07092 | 46.5 | 0.07184 | 198 |
| | 0.07092 | 47.5 | 0.07184 | 188 |
| | 0.007092 | 48.8 | 0.007184 | 205 |
| | 0.007092 | 46.0 | 0.007184 | 189 |
| <i>III</i> | 0.7565 | 5.75 | 0.7564 | 19.7 |
| | 0.0836 | 6.11 | 0.0840 | 16.9 |
| | 0.00836 | 5.51 | 0.0084 | 18.2 |
| <i>IV</i> | 0.7396 | 95.3 | 0.7020 | 462 |
| | 0.0740 | 92.8 | 0.0760 | 392 |
| | 0.0079 | 92.9 | 0.0078 | 362 |

a standard acid solution and a solution of β -diketone HL with a standard hydroxide solution. The measuring cell was calibrated by titration of a perchloric acid standard solution with a sodium hydroxide standard solution for this purpose. The accuracy of the calibration was checked by measuring the ion-product of water; the pK_w equalled 13.73 ± 0.02 (I 0.2, 25°C) in all cases. In titration of HL in a water-benzene system, $K_D = 115$ was obtained ($c_{\text{HL}} = 1.219 \cdot 10^{-2}\text{M}$), or $K_D = 131$ ($c_{\text{HL}} = 4.925 \cdot 10^{-2}\text{M}$); in a water-chloroform system, K_D values of 296 ($c_{\text{HL}} = 1.122 \cdot 10^{-2}\text{M}$) or 355 ($c_{\text{HL}} = 5.866 \cdot 10^{-2}\text{M}$) were obtained. When L^- was titrated in the water-benzene system the values, $K_D = 119$ ($c_{L^-} = 1.169 \cdot 10^{-2}\text{M}$) or $K_D = 68$ ($c_{L^-} = 1.045 \cdot 10^{-1}\text{M}$), were obtained; in the water-chloroform system, a K_D value of 200 was obtained for $c_{L^-} = 1.107 \cdot 10^{-2}\text{M}$ and $c_{L^-} = 1.064 \cdot 10^{-1}\text{M}$.

DISCUSSION

β -Diketones *I-IV* were prepared by Claisen condensation using sodium hydride, which has proven a good condensation agent; its use for the preparation of *I* has not yet been described. By distillation of the reaction product during the preparation of *I*, two fractions, boiling between 75–78°C/18 Torr (colourless) and 96–98°C/

18 Torr (yellow), were obtained. Both fractions form cupric salts sparingly soluble in water. The IR and NMR spectra showed that the latter fraction contained the β-ketoester group; therefore this diketone was purified by preparative GLC. The purification of the other diketones by recrystallization of their cupric salts leads to considerable loss of material, but enables preparation of very pure substances.

The solubility of the diketones in water at 25°C decreases in the order, $II > I > IV$. The solubility of III could not be determined by potentiometric acid-base titration, because of decomposition of the substance with formation of the anion of the acid. On the basis of the volume contraction on mixing III with water and its K_D value, it can be assumed that III is most soluble in water of the studied substances. The solubility of acetylacetone, which is the most common liquid β-diketone, in water at 25°C is $1.7 \text{ mol} \cdot \text{l}^{-1}$ (ref.²²). Hence the solubility of diketones I , II and IV is lower by one order of magnitude. The solubility of I in water has also been determined by Przevalskii and Moiseeva²³; their value (a solubility of 1.5–2% at an undefined temperature) can only roughly be compared with our result (1.3% at 25°C).

As could be expected, the diketone distribution constant values (Table V) increased with decreasing solubility in water in the same order in both the studied systems (water–benzene, water–chloroform), *i.e.* $K_D(III) < K_D(II) < K_D(I) < K_D(IV)$. The distribution constants in the water–chloroform system are always substantially higher than those in the water–benzene system. The distribution constants of I – IV are concentration dependent in both the studied systems, in the studied concentration range ($\approx 8 \cdot 10^{-3} - 7 \cdot 10^{-1} \text{ M}$). The K_D values usually increase with increasing reagent concentration. A greatest change is encountered with diketone IV in the water–chloroform system (K_D increases by 27%); The K_D changes in this system are generally larger than in the water–benzene system. This phenomenon can be explained by the formation of hydrogen bonds between the diketone and chloroform. The large change in the $K_D(IV)$ value with a change in concentration cannot be explained by the formation of intermolecular hydrogen bonds and consequent association of the diketone in the organic phase as might have been assumed. Hydrogen bonding is more probable with greater contents of the enol-form. There is a large content of the enol-form with diketone IV ; however, a substantially smaller change in K_D with changing concentration (an increase by 5%) is encountered with I , which has almost the same content of the enol-form as IV .

The determination of K_D by two-phase titration was unsuccessful here; this verifies the Christiansen condition²⁴ that $\text{p}K_a + \log(1 + K_D) < 11$. This condition is not fulfilled by the studied diketones. Moreover, it has been found²⁵ that the determination of K_D by this method is affected quite strongly by hydrolysis of some component of the system (*e.g.* butylacetate used as the solvent in ref.²⁵). During two-phase titration of diketones I – IV , the diketones can decompose in alkaline media with consumption of OH^- ions leading to disturbance of the material balance. For example, the rate constant of alkaline dissociation of IV was found to be $k = 6 \cdot 10^{-4} \text{ min}^{-1}$

(ref.²⁶), so that after 200 min, which is the time usually required for performing two-phase titration, c_0/c_t equals 1.3, i.e. 11.5% of the diketone *IV* originally present has decomposed. Further, the possibility of extraction of the sodium salts of the diketones must also be considered (ref.²⁷), since otherwise lower K_D values are obtained. From the difference in the K_D values obtained in the titration with acid (diketone transfer from the aqueous to the organic phase) and with base (diketone transfer from the organic into the aqueous phase) it can be concluded that the procedure employed and the stirring time were not sufficient for attaining partition equilibrium.

Light absorption by the studied diketones in the UV region in various media was utilized for their determination during study of distribution and protolytic equilibria. It has been proven that *I–IV* are completely converted to their non-dissociated forms, HL, in 0.05M-HClO₄ and are completely dissociated to L⁻ in 0.05M-NaOH. The absorption maxima of the HL forms of *I–IV* lie from 255 to 288 nm (Table I). The shortest wavelength corresponds to $\lambda_{\max}(II)$, i.e. the maximum of the diketone with symmetrical structure; the longest wavelength, λ_{\max} , is exhibited by diketone *III*, which also has the lowest ϵ_{\max} value. Conversion of HL to L⁻ in solution is manifested by a bathochromic effect, which amounts to 19 nm for all the diketones, *I–IV*. A hyperchromic effect is simultaneously encountered, so that the measurement of light absorption by alkaline solutions of *I*, *II* and *IV* is a sensitive method for their determination. The absorption coefficient of *III* could not be determined, because of its rapid decomposition in alkaline media. The absorbance of the other diketones does not change much over 24 hours, even in alkaline medium (Table II). The HL form was employed for the spectrophotometric determination of *III*; this is, however, poorly sensitive, because of the low value of ϵ_{288} . The relative width of the confidence limits for $\epsilon_{\max}(L^-)$ is 4% for *I*, *II* and *IV*; for $\epsilon_{\max}(HL)$ with *III* it amounts to 7%.

The most important bands in the IR spectra of diketones *I–IV* are located around 1600 cm⁻¹ and 1700 cm⁻¹. The first band can be assigned to the six-membered chelate ring, formed by intramolecular hydrogen bonding in the diketone enol-form. On dissolution in tetrachloromethane, this band shifts somewhat to lower wave numbers (a shift by 10⁻¹ cm⁻¹). Rassmussen and coworkers²⁸ found a similar band for acetylacetone at 1630 cm⁻¹. Since the wavenumber of this band decreases with increasing substituent mass, assignment of the band with the wavenumber, 1600 cm⁻¹, to the enol-form chelate ring is quite certain. The band intensity changes with the diketone type along the series: *IV* > *I* = *II* ≫ *III*.

The other band, at about 1700 cm⁻¹, corresponds to the carbonyl group valence vibration and hence to the diketo-form. Its intensity varies in the series, *III* > *II* = *IV* > *I*. The absorption band of the conjugated carbonyl group, which should appear at 1670–1695 cm⁻¹ (ref.²⁸), was not observed in the spectra of the pure diketones. The absorption band of the free —OH group was also not observed.

Interpretation of the NMR spectra gave the same information and moreover, it made possible determination of the particular carbonyl group of the unsymmetrical

diketones (*I*, *III*, *IV*) on which enolization occurs. According to an empirical rule, enolization should take place on the carbonyl group which is the farthest from the acyl-group, derived from the strongest acid (here from acetyl). With ketones *I–III*, a single tautomeric equilibrium (Scheme A–C) was found by NMR spectroscopy, while for diketone *IV* the possibility of enolization on both carbonyl groups is indicated (Scheme D). The chemical shifts found for the —CH₂— group in the keto-form of *IV* and the —CH= group in the enol-form of *IV* (Table III) are in good agreement with the literature values¹⁶.

The results obtained by IR and NMR spectroscopy indicate that the enol content in the studied diketones varies in the order, *IV* ≈ *I* > *II* > *III*. The content of the enol-form of *IV* in aqueous solution was also determined by NMR spectroscopy; it decreased to 18%. The same value was found by Calmon and coworkers^{7,8} from the UV spectra, while a different value (8.3%) was found iodometrically⁹.

If the same assumption is made as in ref.⁷, *i.e.* that the absorption coefficients at λ_{\max} of the β-diketone enol-forms of similar structures change only slightly with a change in the substituent and lie in the range, 11000–12500, then the following enol contents in aqueous solution can be calculated from ϵ_{\max} in water (Table I): *I* 16–17.6%, *II* 9.0–9.8%, *III* 1.8–2.0%, *IV* 19.2–21%. Therefore, closer values for *IV* were obtained by spectral methods than by the chemical method. The pK_a values of diketones *I–IV* (Table IV) vary in the order, *I* > *IV* > *II* > *III*, the difference between $pK_a(I)$ and $pK_a(IV)$ being smaller than with the other diketones. The pK_a values obtained are generally in good agreement with the values published earlier. For *I*, Calmon and Maroni⁷ found $(pK_a)_T = 9.23 \pm 0.02$ (25°C). They do not mention the second fraction in the reaction product distillation, which has acidic properties, yields a crystalline cupric salt and absorbs strongly at the wavelength employed for the determination of pK_a . Hence the difference between their value and the value found here can be explained. The $pK_a(IV)$ values are also in good agreement with the published values: $(pK_a)_T = 9.43 \pm 0.03$, potentiometry⁶ (25°C); 9.41 ± 0.015 , spectrophotometry⁶ (25°C), 9.40 ± 0.04 , spectrophotometry^{7,8} (25°C). The value of $pK_a(II)$ obtained here differs from the value found by Koshimura and Okubo⁴ (9.55 ± 0.03 , 20°C). Our value (10.04) is closer to the value obtained earlier by Rumpf and Rivière⁹ potentiometrically and spectrophotometrically ($(pK_a)_c = 9.83 \pm 0.02$), especially when it is considered that this value further increases on recalculation to $(pK_a)_T$. The recalculation cannot be carried out, since the ionic strength of the medium is not specified in the paper⁹.

During the potentiometric determination of $pK_a(III)$, two inflexion points were found even after purification of the material and a check by GLC. The diketone apparently decomposes during the titration, with formation of an acidic product with $pK_a \approx 4.8$, *i.e.* probably acetic acid. From the amount of this component, determined by the titration, a correction factor for the decomposed part of *III* was calculated and included in the calculation of pK_a . The $pK_a(III)$ value has not yet been published.

It can be compared with the value for 3-ethyl-2,4-pentanedione: $(pK_a)_T = 11.34 \pm \pm 0.03$ (25°C).

With the β -diketone dissociation constants, some authors^{7,9,29} distinguish between the dissociation constant of the enol-form (K_{HE}) and that of the keto-form (K_{HK}). If the equilibrium constant of the tautomeric equilibrium is denoted as $K_c(\text{HK} \rightleftharpoons \rightleftharpoons \text{HE}) = P/(100 - P)$, pK_{HE} can be calculated from the relation, $pK_{HE} = pK_a + + \log P - 2$. Then the following series of the pK_{HE} values is obtained: *I* (8.57), *IV* (8.73), *II* (9.01), *III* (9.48); this is the same order as with the pK_a values, but the difference in pK_a 's are now smaller, which is more realistic, since weak acids of the same composition and similar structure are involved.

From diketones *I-IV*, diketone *IV* has been chosen for further study, since it bears the greatest promise as a reagent to be deposited on a support for RPPC: it exhibits the lowest solubility in water, has the highest distribution constant in the two systems studied, is sufficiently stable in aqueous media and has a large content of the enol-form. For deposition of *IV* as a stationary phase, benzene is preferable to chloroform as a solvent, since $K_D(\text{IV})$ is smaller in benzene, thus promising faster equilibration in the extraction of metal chelates.

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REFERENCES

1. Stronski I.: *Isotopenpraxis* 9, 273 (1973).
2. Alimarin I. P., Bolshova T. A.: *Pure Appl. Chem.* 31, 493 (1972).
3. Pierce T. B., Peck P. F.: *J. Chromatog.* 6, 248 (1961).
4. Koshimura H., Okubo T.: *Anal. Chim. Acta* 49, 65 (1970).
5. Shikematsu T., Tabushi M., Matsui M., Utsonomiya K.: *Bull. Inst. Chem. Res., Kyoto Univ.* 45, 290 (1967).
6. Laloi L., Rumpf P.: *Bull. Soc. Chim. France* 1961, 1645.
7. Calmon J. P., Maroni P.: *Bull. Soc. Chim. France* 1965, 2525.
8. Calmon J. P., Cazaux - Maraval Y., Maroni P.: *Bull. Soc. Chim. France* 1968, 3779.
9. Rumpf P., La Rivière E.: *Compt. Rend.* 244, 902 (1957).
10. Plešek J., Heřmánek S.: *Sodium Hydride*, p. 110. Academia, Prague 1968.
11. Chaney A., Astle M. J.: *J. Org. Chem.* 16, 57 (1961).
12. Moshier W. R., Sievers R. E.: *Gas Chromatography of Metal Chelates*, p. 145. Pergamon Press, London 1965.
13. Sýkora V., Zátka V.: *Tables for Chemists*, 3rd Ed., p. 65. Published by SNTL, Prague 1967.
14. *Analytical Absorption Spectroscopy* (M. G. Mellon, Ed.), p. 261. Wiley, New York 1950.
15. Walker I. K., Todd H. J.: *Anal. Chem.* 31, 1603 (1959).
16. Schweitzer G. K., Benson E. W.: *J. Chem. Eng. Data* 13, 452 (1968).
17. Lochmueller C. H., Maldacker T., Cefola M.: *Anal. Chim. Acta* 48, 139 (1969).

18. Eckschlager K.: *Errors of Chemical Analyses*, 2nd Ed., p. 124. Published by SNTL, Prague 1971.
19. Eistert B., Reiss W.: *Ber.* 87, 116 (1954).
20. Dyrssen D.: *Acta Chem. Scand.* 9, 763 (1955).
21. Dyrssen D.: *Svensk. Kem. Tidskr.* 64, 213 (1952).
22. Steinbach J. F., Freiser H.: *Anal. Chem.* 26, 375 (1954).
23. Przevalskii E. S., Moiseeva L. M.: *Vestn. Mosk. Univ., Ser. Mat. Mech. Astron. Fiz. Chim.* 14, 203 (1959).
24. Christensen J. A.: *Acta Chem. Scand.* 16, 2363 (1963).
25. Vláčil F.: *Thesis*. Institute of Chemical Technology, Prague 1966.
26. Calmon J. P., Maroni P.: *Bull. Soc. Chim. France* 1968, 3761, 3772.
27. Guter G. A., Hammond G. S.: *J. Am. Chem. Soc.* 78, 5166 (1956).
28. Rassmussen R. S., Tunnicliff D. D., Brattain A. R.: *J. Am. Chem. Soc.* 71, 1068 (1949).
29. Schwarzenbach G.: *Helv. Chim. Acta* 23, 1147 (1940).

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