

Determination of Acidic Dissociation Constants in the Row of Methoxy- β -Diketones Using Electron Transition Energies of the Corresponding Chelates

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Abstract

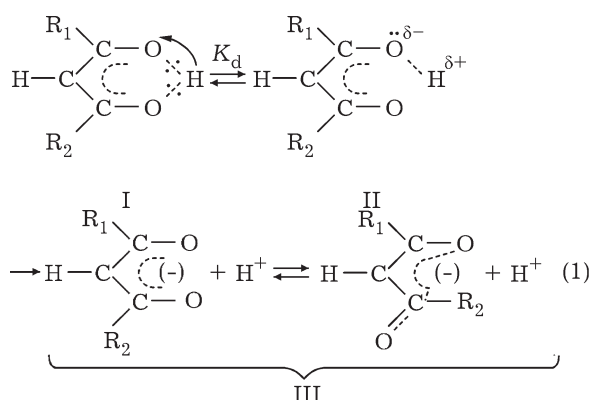
A new technique of the determination of acidity index pK_d in the rows of analogous chelating organic compounds is proposed and described. The technique is based on determining the energy of electron transitions in the corresponding metal complexes. The technique was tested with β -diketones $R^1-CO-CH_2-CO-R^2$ where R^1 , R^2 are alkyl and fluoroalkyl fragments exhibiting different induction effect. Tests with the diketones characterized by the known acidic dissociation constants demonstrated the possibility to achieve an accuracy within the range 0.1 – 0.05 pK_d . The technique was used to arrange ten synthesized methoxy- β -diketones into acidity row and to estimate their acidic dissociation constants. The technique can also be used for the predictions in selecting initial compounds for film deposition in the simultaneous synthesis-transport of metal complexes.

INTRODUCTION

The development of solid-gas phase synthesis of metal organic and metal complex compounds puts forward a very important problem of the predicted selection of reagents according to the parameters of their chemical interaction. In particular, relatively new technology of the deposition of thin films of metal-containing compounds during the simultaneous synthesis-transport [1] includes the stage of phase (surface) etching of the solid complex metal oxide in the flow of volatile chelate forming ligand vapour. The rate of oxide etching and the corresponding rate of chelate formation are determined, in particular, by gas-phase acidity of the ligand which, in turn, directly correlates with the acidity index pK_d of the ligand in liquid [2]. So, this parameter, determined by one method or another, can serve as one of the basic indicators of the efficiency of chelating ligand during the deposition of films according to the mentioned technology of simultaneous synthe-

sis-transport. To know pK_d of the synthesized ligands is also of fundamental importance.

Existing methods of the determination of acidic dissociation constants are based, directly or indirectly, on the measurement of the concentration of either hydrogen ions or the conjugated anion. This limits the possibility to determine dissociation constants, first of all for poorly dissociated compounds, *i. e.* in the region where pK_d of the ligand are comparable with, or exceed, pK_d of the solvent, second, for easily solvolyzed (hydrolyzed) compounds, for example, polyfluorinated β -diketones like hexafluoroacetylacetone. At the same time, electronic absorption spectra of the solutions of metal complex compounds exhibit a monotonous, nearly linear dependence of the energy of electronic charge-transfer transitions (CTT) ΔE on pK_d of ligands in chelate complexes, while for $\pi-\pi^*$ this monotonous behaviour is not observed [3]. In the case if the ligands are β -diketones, the reason is common character of dynamic processes in-



volving electron density redistribution in the molecule during acidic dissociation of the enole form of the ligand and during the excitation of electronic transitions in metal chelate.

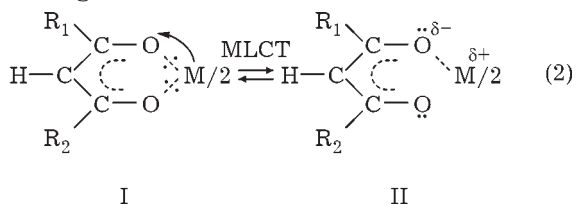
This regularity is usually applied to assign charge-transfer transitions in metal complexes [3, 4]. We believe that it can also be used to determine acidic dissociation constants in the rows of similar ligands on the basis of spectral characteristics of metal complexes formed by these ligands. It is sufficient to rely upon the substances with pK_d known from literature and to build up a reference linear dependence $\Delta E = L(pK_d)$ and then to compare it with the measured spectral parameters of the solutions of chelates under investigation. Along with the simplicity of this procedure, its additional advantage is the fact that thus determined pK_d values do not depend on solvent in which the spectral parameters of the chelates are determined (this solvent should just be one and the same for the entire row, including reference substances), but depend only on the basic set of pK_d for the reference substances and relate to a medium for which this basic set was obtained.

The goal of the present study was to develop a technique for the determination of acidic dissociation constants in the row of similar β -diketones $R^1\text{-CO-CH}_2\text{-CO-R}^2$ (R^1 and R^2 are α -substituents) using the energies of electronic transitions in the corresponding metal complexes, and to test this technique in estimating pK_d of a series of the synthesized methoxy- β -diketones.

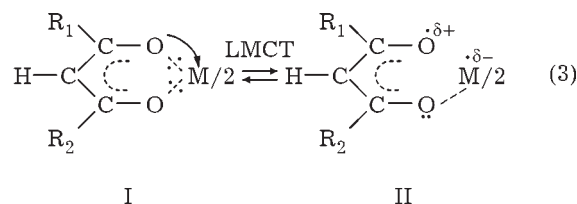
According to the existing notions [5], enolic form of β -diketone is a symmetrical monoligand hydrogen chelate (intramolecular hydrogen bond with oxygen atoms in the ketoenolic ring).

Acidic dissociation of this form involves thermally activated equilibrium charge transfer from s -orbital of hydrogen atom to p - (or conjugated p - π) orbital of the oxygen fragment of ketoenolic ring (reaction (1)). "Equilibrium transfer" here means that the electronic density redistribution is accompanied by the rearrangement of nuclei and reorganization of the medium (resolution). It should also be noted that in this case, besides the slow (limiting) stage of thermally activated electron transfer (1)-I \rightarrow (1)-II, the equilibrium reaction of acidic dissociation includes also the stage of the stabilization of transition state (1)-II \rightarrow (1)-III with the formation of anion that undergoes *cis-trans* rearrangement (a configurational analogue of the p - π^* transition in the anion) [6]. The free energy of the equilibrium acidic dissociation $-\Delta G$ by its absolute value is equal to $2.3RT \cdot pK_d$, *i. e.* an equilibrium energy increment $S_e = |d\Delta G/dpK_d| = 0.48$ kK.

Similarly, the excitation of the electronic charge-transfer transition from metal to ligand (MLCT) in metal chelates is accompanied by vertical electron transfer in the same direction from metal orbitals to the oxygen fragment of the ligand:



Dipole moment thus increases, as it does in the dissociation of ketoenol, and the transition energy ΔE increases with increasing pK_d of the ligands due to an increase in the induction effect of α -substituents which shifts the energy level of the orbitals of oxygen fragment in the ketoenolic ring. When the ligand-to-metal charge-transfer transition band (LMCT) is excited, electron transfer occurs from the orbitals of the oxygen fragment in ligand to metal orbitals, and the dipole moment of chelate molecule is changed inversely:



It is easy to note that the transformation (3)-I \rightarrow (3)-II is similar in the dynamics of electronic configuration changes to the process reverse to the stage (1)-II \rightarrow (1)-I of equilibrial dissociation, *i. e.* the energy of LMCT changes in phase with $1/K_d$. Correspondingly, LMCT energy decreases with increasing pK_d in the same row of compounds. So, the dependence of charge transfer band energies in chelates on pK_d of ligands should be monotonous. Really, experimental data confirm that this dependence is close to linear. This is likely to be conditioned by the fact that, on the one hand, the limiting stage of thermally activated dissociation is intramolecular electron transfer, on the other hand, the contribution of cis-trans anion rearrangement energy is slightly varied with variation in the induction effect of α -substituents therefore with pK_d and thus it is practically identical over the whole row of ligands.

EXPERIMENTAL

In the present study the proposed technique is tested using the reference copper and barium β -diketonates (LMCT [3] and LMCT [7], respectively); with copper chelates, acid dissociation constants are estimated for 10 synthesized β -diketones with alkyl, fluoroalkyl and methoxyalkyl α -substituents. Though much better accuracy of pK_d determination (till 0.1 – 0.05 pK_d) was achieved using reference dependences for barium chelates, we did not succeed in using barium because of the difficulties connected with the preparation of barium chelates with new ligands. We did not test ligands with aromatic α -substituents because, due to strong influence of the aromatic α -system, they fall off the general correlation and, most likely, require the use of other basic set of reference substances.

In order to obtain the reference linear dependencies $\Delta E = L(pK_d)$, we selected well-known copper (II) and barium β -diketonates that were synthesized according to [8] and repeatedly sublimed in vacuum. The following β -diketones with well-known pK_d were used as the ligands for these chelates: acetylacetone (HAA), dipivaloylmethane (HDPM), trifluoro-

acetylacetone (HTFA), pivaloylacetone (HPA), and pivaloyltrifluoroacetone (HPTA). Chelate powder was dissolved in ethanol at room temperature (concentration: $\sim 10^{-4}$ M). UV absorption spectra of the solutions within the range 200–360 nm were registered using an automated optical spectrophotometer [9].

Methoxy- β -diketones were synthesized by us according to the technique described in [10]. Since we needed only spectral characteristics of the new chelates as the initial information to calculate pK_d , we used a simplified technique synthesizing the chelates directly in the samples under investigation. For this purpose, small weighed portions of the ligands were dissolved in ethanol (20 ml) in a tight glass vessel; $\text{Cu}(\text{OH})_2$ was added in excess and the vessel was placed in a thermostat at a temperature maintained about 60 °C. In some cases, in order to accelerate the formation of chelates, we added NH_3 . The amount of initial reagents in the sample was specified so that the chelate concentration after the synthesis could be $\sim 10^{-4}$ M. In spite of substantial synthesis time consumption (sufficient transformation degree was achieved within 2–4 weeks), this technique allowed to use minimal amounts of expensive reagents and avoid labour-consuming traditional synthesis in solutions. Advancement degree of the chelation reaction was monitored with UV absorption spectra of solution recorded with the spectrophotometer at regular intervals. The accumulated digital files of spectral data were processed statistically with an IBM computer using Microcal Origin 5.0.

RESULTS AND DISCUSSION

Some typical UV absorption spectra of copper β -diketonate solutions are shown in Fig. 1. In literature, a low-frequency band in the spectrum

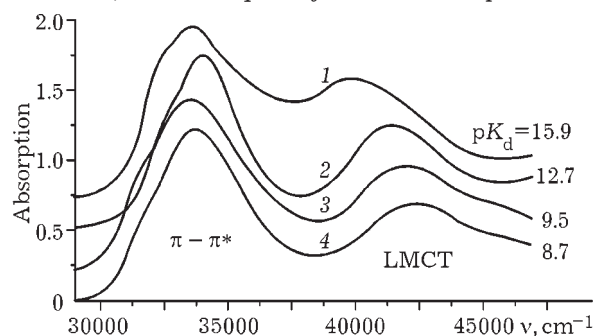


Fig. 1. UV absorption spectra of copper chelate $\text{Cu}(\text{L})_2$ solutions in ethanol. L = DPM (1), AA (2), PTA (3), TFA (4).

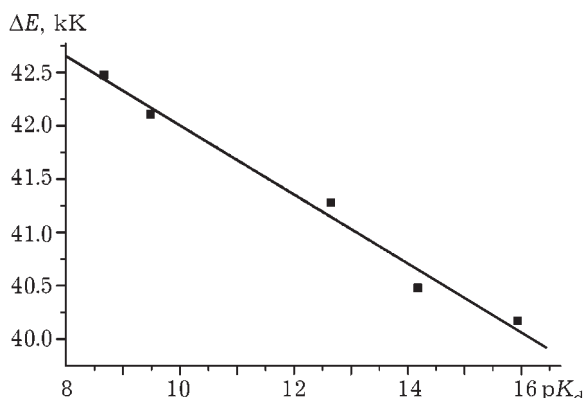


Fig. 2. Calibration dependence for the reference β -diketones.

of copper chelate is attributed to intraligand π - π^* transition while the high-frequency band is attributed to LMCT [3]. The position of the second band ΔE is decisive for the determination of pK_d . The obtained dependence $\Delta E = L(pK_d)$ for a series of reference chelates is shown in Fig. 2. One can see that the dependence is linear with a slope $S = d\Delta E/dpK_d = -0.33 \text{ kK}$ and high linear correlation coefficient $R \geq 0.993$. The observed coincidence of the slope S with the equilibrium energy increment S_e within a factor of 2 points to not very substantial contribution from unaccounted energy-exchange processes. Using the correlation dependence $pK_d = 138.04 - 3.05\Delta E$ obtained for reference substances, we calculated acidity indices of the

methoxydiketones under investigation. Statistical treatment of the data gives mean square standard deviation SD for the pK_d to be 0.4.

The calculated acidity indices for ten new methoxy- β -diketones are shown in Table 1 in comparison with acidity indices of the reference diketones. The energies of charge-transfer transitions for copper chelates are also shown there. A most detailed and precise list of pK_d of the reference diketones in water-dioxane mixtures (dioxane 74.5 %) is given in [3, 11].

CONCLUSION

The novel technique proposed by us allows rather simple determination of acidity indices of newly synthesized β -diketones and the use of this basis to select chelating ligands that would be promising for the technology of oxide film deposition using the simultaneous synthesis-transport. The acidity is determined for ten new methoxy- β -diketones that were not investigated earlier. The data obtained can be used for correlation estimates of the parameters of chelate formation in gas phase and in solution, the heat of chelate decomposition, with the limiting stage being ligand abstraction, as well as other thermodynamic parameters that can be connected with pK_d through the Hess cycle.

TABLE 1

Experimental data for reference compounds and synthesized β -diketones $R^1\text{-CO-CH}_2\text{-CO-R}^2$

Ligand	R^1	R^2	ΔE_{CTT} for copper chelate, kK	pK_d
<i>Reference diketones</i>				
HDPM	<i>tert</i> -Butyl	<i>tert</i> -Butyl	40.16	15.9*
HPA	»	Methyl	40.47	14.2*
HAA	Methyl	»	41.26	12.7*
HPTA	<i>tert</i> -Butyl	Trifluoromethyl	42.19	9.5*
HTFA	Methyl	»	42.46	8.7*
<i>Synthesised diketones</i>				
HZIS ₁	Dimethylmethoxy methyl	<i>tert</i> -Butyl	39.10	18.9
HZIS ₂	»	Isopropyl	39.40	18.0
HZIS ₃	»	Hexyl-2	39.63	17.3
HZIS ₈	Methylhexylmethoxymethyl	<i>tert</i> -Butyl	39.20	18.6
HZIS ₉	»	Isopropyl	39.83	16.6
HZIS ₁₀	»	Hexyl-2	39.10	18.9
HZIS ₁₇	1-Methoxycyclohexyl-1	Isopropyl	38.90	19.5
HZIS ₂₀	»	Trifluoromethyl	41.30	12.2
HZIS ₂₁	Methyl- <i>tert</i> -butyl methoxymethyl	Isopropyl	39.40	18.0
HZIS ₂₂	1-Isopropyl-2-methyl-2-methoxyethyl-2	»	39.30	18.3

*The data are taken from [3, 11].

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