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INFLUENCE OF ULTRAVIOLET LIGHT ON SOME COPPER CHELATES OF β -DICARBONYL COMPOUNDS

SPECTRAL EVIDENCE FOR A PHOTOACTIVATED METALLOTROPY

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Summary

The influence of ultraviolet light on heptane solutions of the copper chelates of several β -dicarbonyl compounds has been followed by spectroscopy. Reversible transformations are apparent, leading us to assume the presence of a photoactivated metalotropy.

Introduction

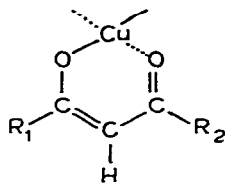
Light-induced transformations of β -dicarbonyl compounds have been the subject of recent intensive studies [1–5]. It was found that under the influence of UV irradiation the keto–enol equilibrium is shifted towards the keto form. On the other hand, studies involving magnesium [6,7] and copper [8] derivatives of ethylacetoacetate, as well as several other metal chelates of enolizable compounds [9–11], have established the presence of metalotropy of these compounds solution. With regard to these facts, it was of interest to consider the influence of ultraviolet irradiation on some chelates of β -dicarbonyl compounds dissolved in nonpolar solvents. The present work is concerned with the extension of our preliminary studies in this field [12].

Results

The UV, IR and EPR spectra of heptane solutions of the copper chelates I–XXI have been examined.

UV spectral data

In some cases, rather surprisingly, compounds I–VII, a significant spectral change occurs in the course of time after dissolving the copper chelate. The



	R ₁	R ₂		R ₁	R ₂
(I)	CH ₃	OC ₂ H ₅	(XI)	<i>p</i> -ClC ₆ H ₄	OC ₂ H ₅
(II)	C ₂ H ₅	OC ₂ H ₅	(XII)	<i>p</i> -CH ₃ C ₆ H ₄	OC ₂ H ₅
(III)	CH ₃ (CH ₂) ₃	OC ₂ H ₅	(XIII)	<i>p</i> -BrC ₆ H ₄	OC ₂ H ₅
(IV)	CH ₃ (CH ₂) ₄	OC ₂ H ₅	(XIV)	CH ₃	OC ₅ H ₁₁
(V)	CH ₃ (CH ₂) ₈	OC ₂ H ₅	(XV)	CH ₃	OCH ₂ (CH ₂) ₆ CH ₃
(VI)	(CH ₃) ₂ CHCH ₂	OC ₂ H ₅	(XVI)	CH ₃	OCH ₂ (CH ₂) ₈ CH ₃
(VII)	C ₆ H ₅ CH ₂	OC ₂ H ₅	(XVII)	CH ₃	OC ₆ H ₁₁
(VIII)	C ₆ H ₅	OC ₂ H ₅	(XVIII)	CH ₃	OCH ₂ C ₆ H ₅
(IX)	<i>m</i> -CH ₃ C ₆ H ₄	OC ₂ H ₅	(XIX)	CH ₃	OCH=CHC ₆ H ₅
(X)	<i>m</i> -CH ₃ OC ₆ H ₄	OC ₂ H ₅	(XX)	CH ₃	CH ₃
			(XXI)	C ₆ H ₅	CH ₃

observed alterations in the UV spectrum of I are presented in Fig. 1. The UV spectral data for compounds I–XXI, together with those for the corresponding β -dicarbonyl compounds are collected in Table 1. The stabilized (constant UV spectral characteristics with time) heptane solutions were irradiated with 254 nm (compounds I–VII, XIV–XIX) and 313 nm (compounds VIII–XIII) monochromatic light. In all cases irradiation resulted in profound spectral changes (Figs. 2 and 3). The concentrations of compounds I–VII and XIV–XIX gradually decrease on lengthening the irradiation period. In the case of chelates VIII–XIII, the spectral change in the 280–300 nm region is accompanied by the appearance of new absorption maxima (240–260 nm).

The observed UV spectral data were used to determine values for the molecular extinction coefficients ϵ_{250} , ϵ_{290} of two metalotropic (see discussion) forms

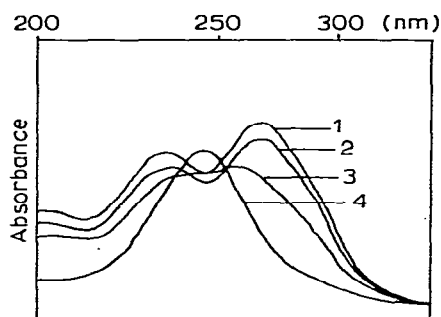


Fig. 1. UV spectra of chelate I in heptane (ca. 0.5×10^{-4} M) measured at different times after solution (1) 0, (2) 1, (3) 7, (4) 20 h.

TABLE I
UV ABSORPTION DATA FOR COMPOUNDS I–XXI AND THE RELATED β -KETOESTERS ^a

Compound	λ (nm)	β -Ketoester		
		β -Ketoester	Copper chelate	
			Freshly prepared solution	Stabilized ^b solution
I	242		233, 267	243
II	246		235, 267	246
III	246		236, 264	247
IV	246		236, 268	250
V	246		235, 260	249
VI	247		233, 260	245
VII	252		248, 270	250
VIII	242, 290		243, 295	
IX	242, 290		252, 294	
X	251, 286		250, 295	
XI	245, 292		248, 295	c
XII	251, 286		265, 300	
XIII	258, 294		252, 298	
XIV	246		234, 265	245
XV	242		232, 270	247
XVI	244		234, 260	245
XVII	245		232, 270	245
XVIII	247		234, 269	248
XIX	255		257	
XX	272		249, 300	c
XXI	249, 309		258, 323	

^a 1×10^{-4} mol l⁻¹ heptane solutions. ^b Average equilibrium time, 7 days. ^c No change of UV characteristics with time.

of compounds VIII–XXI, following the method of Varma. The linear dependences between the absorbances at 290 nm (A_{290}) and 250 nm (A_{250}) of compounds VIII–XIII, measured after different durations of UV irradiation, are given in Fig. 4. The points of intersection of the extrapolated straight lines and

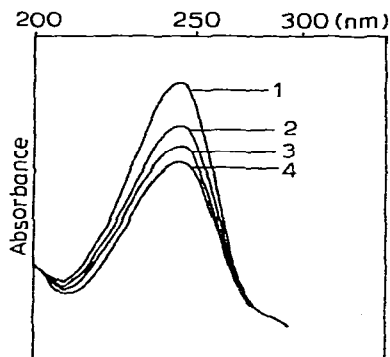


Fig. 2. UV spectra of chelate I in heptane (ca. 0.5×10^{-4} M) at different times after the start of the UV (254 nm) irradiation.

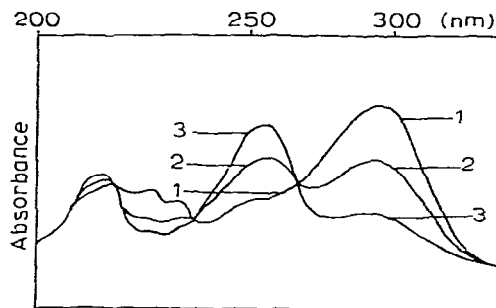


Fig. 3. UV spectra of chelate XI in heptane (ca. 0.5×10^{-4} M) at different times after the start of the UV irradiation (313 nm).

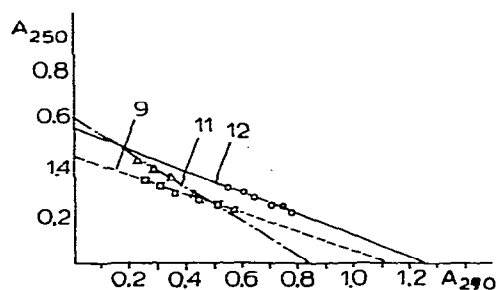


Fig. 4. Dependence between the absorbances A_{250} and A_{290} of compounds IX, XI and XII measured at different times after the start of UV irradiation (313 nm). Initial concentrations $0.5 \times 10^{-4} M$ (heptane).

the coordinate axis give the numerical values of the extinction coefficients of the respective metalotropic forms. The calculated values of ϵ_{250} and ϵ_{290} as well as the oscillator strengths of chelated forms VIII–XIII are presented in Table 2.

It seems reasonable to assume that atmospheric oxygen may take part in the photoactivated transformations observed. In order to check this assumption, two parallel experiments using aerated and deaerated solutions of I have been performed. The data obtained showed no difference in the final results.

The spectral changes due to the irradiation are reversible. The original spectral features of the solutions are restored in the dark at rates which vary widely for the different compounds of various concentrations. In the cases when dilute heptane solutions ($1 \times 10^{-4} \text{ mol } \Gamma^{-1}$) were irradiated with monochromatic UV light, the reversibility observed does not depend on the duration of the initial irradiation. But prolonged irradiation (120 h) of concentrated solutions of I, IV and VII with high intensity polychromatic light leads to the gradual formation of a pale green crystalline product, insoluble in ordinary organic solvents. The UV spectrum of a methanol solution of the isolated product consists of two maxima at 245 and 275 nm.

Irradiation of a heptane solution of compound XX with monochromatic light (313 nm) leads to minor changes in its spectral characteristics. The solution of the copper complex of benzoylacetone (XXI) is more sensitive towards UV irradiation.

The kinetics of the phototransformation observed was studied using dilute ($1 \times 10^{-4} \text{ mol } \Gamma^{-1}$) heptane solutions of I–XIX. In all cases the experimental data

TABLE 2
CALCULATED EXTINCTION COEFFICIENTS AND OSCILLATOR STRENGTH FACTORS OF CHELATES VIII–XIII

Compound	ϵ_{290}	ϵ_{250}	f
VIII	34800	14800	0.9
IX	43600	17600	1.0
X	40000	11600	1.0
XI	34000	23200	0.9
XII	47000	13600	1.0
XIII	29400	16000	0.7

TABLE 3^a

RATE CONSTANTS (k) AND QUANTUM YIELDS (ϕ) OF THE PHOTOACTIVATED METALOTROPY IN HEPTANE SOLUTIONS OF COMPOUNDS VIII–XIII, MEASURED BY UV SPECTROSCOPY

Compound	k	ϕ
VIII	0.27	0.026
IX	0.27	0.017
X	0.28	0.025
XI	0.28	0.025
XII	0.15	0.020
XIII	0.37	0.029

^a Exciting irradiation, 313 nm.

satisfy a second order rate equation:

$$\frac{1}{C_t} - \frac{1}{C_0} = kt$$

where C_0 denotes the initial concentration of the chelate form and C_t is the concentration t seconds after the beginning of the kinetic run. A plot of $1/C_t - 1/C_0$ against t shows the existence of a good linear relationship. The numerical values of the rate constant k (Table 3) for compounds VIII–XIII have been determined by statistical analysis of each set of experimental data. It proved difficult to calculate the concentrations C_0 and C_t of the remaining copper chelates because of the lack of reliable experimentally determined extinction coefficients. That is why the values of the respective absorbances A_0 and A_t were used. The results reveal that also in these cases the photoactivated transformation follows second order kinetics. The quantum yields were determined according to the literature method [13].

IR spectral data

The main absorption bands in the 6μ region of the crystal forms (nujol) of compounds I–XIX are those at 1530 and 1600 cm^{-1} . It was found that the increase in the length of the carbon chain (compounds I–V) or its branching (VI) does not lead to a substantial change in the characteristic IR bands.

Irradiation of cyclohexane ($2.5 \times 10^{-3} \text{ mol l}^{-1}$) solutions of compounds I–VII and XIV–XIX with monochromatic light (254 nm) causes profound changes

TABLE 4

CHARACTERISTIC BANDS (cm^{-1}) IN THE IR SPECTRA OF I AND I' (NUJOL)

I	I'
—	1720
1600	1620
1540	1570
1295	1295
1170	1180
1070	1070
1030	1030
980	980

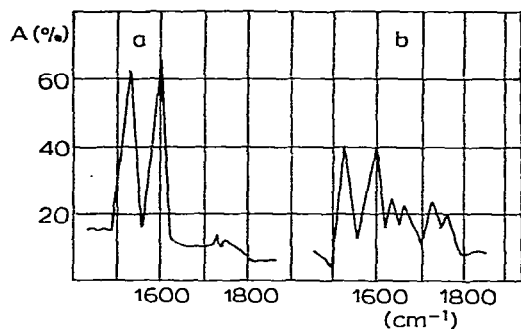


Fig. 5. IR spectra of 0.5×10^{-3} M heptane solution of compound I (a) before irradiation, (b) after 120 min irradiation.

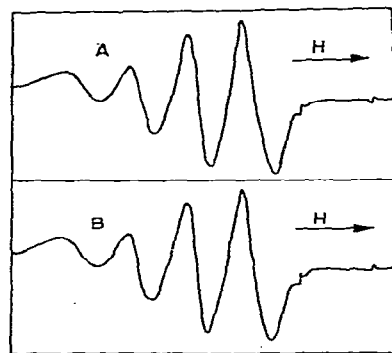


Fig. 6. EPR spectra of a saturated heptane solution of compound I. (A) before irradiation, (B) after 180 min irradiation.

in their IR spectra. The strong IR absorptions near 1530 and 1600 cm^{-1} , attributed to the chelated copper complex, decreases in intensity during irradiation, while the intensity of the 1720 and 1740 cm^{-1} absorption bands increases. Accordingly, new maxima appear at 1640 and 1660 cm^{-1} (Fig. 5). The IR spectra of solutions of copper chelates VIII–XIII have not been studied because of their insolubility in suitable organic solvents.

Some of the basic IR data for product I' formed as a result of prolonged polychromatic irradiation, together with those of the initial product I are given in Table 4.

EPR spectral data

The EPR spectra of a saturated heptane solution of I before irradiation (Fig. 6a) and after successive 120 min irradiation (254 nm) of a deaerated solution of the same compound are shown in Fig. 6.

Discussion

Two different types of UV spectra can be distinguished, depending on the type of the organic component of the copper chelate (Table 1). Freshly prepared solutions of I–VII and XIV–XIX are characterized by the presence of two absorption bands in the ranges 230 – 240 and 260 – 270 nm, merging gradually to one maximum at about 250 nm. On the other hand, compounds VIII–XIII possess two maxima near 240 and 295 nm which do not alter in the course of time. Also, it can be seen that the UV absorption band of the copper chelate closely resembles that of the respective β -dicarbonyl compound. The spectral data for VIII–XIII show the high intensity due to the chelate absorption in the region 280 – 200 nm ($\epsilon \approx 3 \times 10^4$) in relation to the absorbance of β -dicarbonyl compounds ($\epsilon \approx 10^4$).

Belford et al. [14] measured the UV spectrum of I in chloroform and reported a maximum at 254 nm, which they attributed to the $\pi \rightarrow \pi^*$ transition in the CO conjugated ethylene system (chelate form). Their basic argument is the

virtually identical positions of the absorption maxima for I and ethylacetoacetate. Substantially different results were reported by Sen and Thankarajan [15], who reported two bands at 239 and 269 nm. Morton et al. [16] showed that a maximum at 274 nm is typical for the spectrum of I in methanol.

The marked inconsistency of the UV spectral data for the copper chelates under consideration can be explained to a certain degree by the observed spectral changes ensuing in the course of time. The initial spectra of heptane solutions of I–VII correspond closely to the data given by Sen and Thankarajan. On the other hand, the final spectral picture (see Table 1) conforms with the results reported by Belford et al.

Efforts to attain a theoretical interpretation of the UV spectra of copper chelates of some β -dicarbonyl compounds have been made by Basu and Chatterji [17]. However, at present there exists little or no theoretical grounds for the elucidation of the experimental results. Previously the Pariser–Parr–Pople SCF-CI scheme [18] and CNDO/S method [19] were used to investigate theoretically the ground and excited state properties of the enol form of acetoacetic acid. The energy of the $\pi \rightarrow \pi^*$ transition, calculated for the *cis*-enol (chelate) form was 5.00 eV (248 nm). It has been shown, both theoretically [19] and experimentally [20], that the "open" (non-chelated) form exhibits $\pi \rightarrow \pi^*$ transition at 5.44 eV (228 nm). On the basis of the above results it becomes evident that the absorption at 254 nm, found by Belford et al. in the UV spectrum of I, should be attributed to the respective conjugate chelated form. Consequently, it can be concluded that the initial conformation of freshly prepared heptane solutions of the molecules I–VII and XII–XIX is different from that of the chelated form (254 nm), and is spectroscopically described by the absorption at 230 and 270 nm. The appearance of an intensive absorption peak at 270 ± 5 nm in the freshly prepared solutions of I–VII and XIV–XIX can be connected with the presence of species characterized by a prevailing ionic bonding between the organic ligand and the copper. This suggestion gains support from the frequencies reported [21] in the UV spectrum of the anionic form of ethylacetoacetate which possesses a band of 270 nm. It seems that this form has a remarkable stability in polar solvents, which is consistent with the data given by Morton et al. As for the UV absorption at 230 nm, one can assume that it is related to the existence of "open" (non-chelated) enolate structures.

From this standpoint, the spectral changes observed by us can be rationalized as a reflection of a step process of formation of a chelated conjugate system via species of anionic and non-chelated type. The influence of the alkoxy group (R_2) on the rate of this transformation and the accelerating effect of UV irradiation established in the present study, show that the observed changes are undoubtedly related to the presence of a barrier to internal rotation, which is dependent on the bulkiness of the radical R_2 .

As was pointed out, the more prolonged monochromatic irradiation with light of wavelength corresponding to the maximal absorption of the respective copper complex (stabilized heptane or cyclohexane solution) causes a gradual decrease in the concentration of the chelated form. In the case of chelates VIII–XIII, the diminishing intensity in the 280–310 nm region of the UV spectra is accompanied by the appearance and enhancement of a new absorption band at 245–255 nm. It was of interest to compare the UV characteristics of the

copper chelates VIII—XIII before and after UV irradiation, with those of the parent β -dicarbonyl compounds [22]. It is reasonable to expect a similarity in the observed spectral changes. In fact these alterations are virtually the same. Following this line of reasoning one may conclude that the copper chelate (UV absorption 280—300 nm) exists in equilibrium with the carbeniate form (UV absorption 245—250 nm). The successive UV irradiations shift the equilibrium towards the carbeniate form. The presence of isobestic points in the UV spectra of irradiated solutions of VIII—XIII and the linear relationship (Fig. 4) found between the absorbances of the two forms also support this assumption. As far as the IR spectra of these compounds are concerned, there is no proof for the existence of the enolate form.

These facts, as well as the data obtained for chelates I—VII and XIV—XIX by IR spectroscopy, reveal the existence of metalotropy in heptane or cyclohexane solutions of the copper derivatives considered. In this connection it should be noted that a presence of the equilibrium:



has been verified for chloroform solutions of magnesium ethylacetoacetate [6]. An IR spectral investigation of the carbeniate form of some metal complexes of β -dicarbonyl compounds has subsequently been made [23,24]. It was found that spectral bands due to C=O absorption above 1600 cm^{-1} are related to a non-conjugated carbonyl function, showing the existence of a direct link between the carbon and metal atoms. This is in good agreement with the results obtained by other authors [25]. For example, the formation of a copper derivative of cyanoacetic acid possessing a direct carbon—copper bond has recently been demonstrated by Marsich et al. [26].

The comparative experiments (with and without UV irradiation) unequivocally show that the process of metalotropy in solutions of chelates I—XIX proceeds much faster under UV irradiation. As a result of irradiation, the equilibrium:



is quickly shifted towards the enolate ($1630, 1650\text{ cm}^{-1}$) and carbeniate ($1720, 1740\text{ cm}^{-1}$) forms (Fig. 5). Practically the same quantities of the metalotropic forms (measured by IR spectroscopy) have been detected after 8 h of UV irradiation and 100 days without UV irradiation.

As was pointed out, the spectrophotometric assay of the irradiated solutions after irradiation shows a gradual restoration of the chelate content. This reversibility implies that no destructive reduction of the copper chelates ensues under the chosen experimental conditions (non-polar solvents, monochromaticity, intensity and duration of irradiation). The EPR spectrum of I gives further support in this sense. As can be seen from Fig. 6, the quantity of bivalent copper in the solution remains unchanged even after prolonged UV irradiation. It is obvious that our results differ substantially from the data concerning the influence of UV irradiation of the alcohol solutions of copper derivatives of acetylacetone and some other β -diketones [27,28].

It is as yet difficult to rationalize the effect of UV light on the metalotropic equilibrium of copper derivatives of β -dicarbonyl compounds in solution. The available experimental data do not allow us to discuss the possible involve-

ment of electronically excited states of the metal chelate in the process of photoactivated metalotropy. So far as this transformation goes as a thermal reaction, it seems rather probable that UV light causes some distortions of the initial chelated system. One can assume that the "open" enolate form is the resulting species. This assumption implies that the rate of photoactivated metalotropy must depend on the stability of the respective metal chelate. This was, in fact, been found to the case with chelate XX. It is known that metal derivatives of acetylacetonone possess appreciable stability due to the high symmetry of their molecules.

Following the classical ideas [29] concerning the mechanism of the tautomeric rearrangements, the phenomenon observed would be explained as an intramolecular cation migration from an oxygen to a carbon atom and vice versa with the intermediate formation of a mesomeric anion. The experimental data, however, satisfy a second order rate equation (Table 3). It therefore seems reasonable to postulate a mechanism involving the participation of two chelate molecules.

The dependence of the rate of photocativated metalotropy on some structural peculiarities of the ligand system cannot be clearly traced. A correlation exists between the values of the rate constants and the respective quantum yields. The substitution of electron-releasing atoms or groups on the *para* position of the benzene ring tends to increase the oscillator strength due to lengthening of the conjugate system.

The prolonged UV irradiation of heptane solutions of I leads to the formation of a pale green crystalline product I'. The data collected in Table 4 shows that the IR spectral characteristics (nujol) of the initial (I) and final (I') products are very similar. The only important difference consists of the presence of an additional band at 1720 cm^{-1} in the IR spectrum of I'. The nature of the isolated crystalline product remains unexplained at present. The presence of a direct copper-carbon bond is inferred from the marked features of their IR spectra [23].

Experimental

Compounds I-XXI were produced according to ref. 30, and purified prior to use to a purity of 99% or higher. Heptane was spectroscopic grade. The concentrations of solutions investigated are given in the text. The solutions were prepared and kept in the dark. The samples (2 ml) of these solutions were thermostated at 20°C in a quartz glass vessel and exposed to UV irradiation of wavelengths 254 nm (compounds I-VII and XIV-XIX) and 313 nm (compounds VIII-XIII and XX-XXI) under standard conditions. The light quanta falling into the quartz cell (1 cm) were determined by using a uranyl oxalate actinometer.

The UV absorption spectra were measured on a Specord-UV-VIS spectrophotometer using quartz cells 0.5, 1.0 and 2.0 cm wide. The data obtained were recalculated for a cell width of 1.0 cm. The IR spectra were measured on an IR-10 double beam spectrophotometer Carl-Zeiss Jena. EPR spectral data were obtained with a JEOL JES 3RS spectrophotometer.

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