Thermochromism of Metal Chelates with Triphenylmethane Complexons in Aqueous Solutions. I. Copper(II)-Xylenol Orange System[†]

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Reversible thermochromisms are found for about thirty kinds of metal complexes of triphenylmethane complexons in aqueous solutions. The thermochromism observed in the aqueous solution of copper(II) complex with 3,3′-bis[*N*,*N*-bis(carboxymethyl)aminomethyl]-*o*-cresolsulfonphthalein (Xylenol Orange, XO) was primarily ascribed to the temperature-dependence of the protolytic equilibria between a complex species AH having an uncoordinated free phenolic hydroxyl group and a complex species A having a coordinated phenolate group: $AH \rightleftharpoons A+H$. The equilibrium constant K of the reaction was determined to be $p(K/\text{mol dm}^{-3})=4.40$ at 25 °C. The thermodynamic parameters ΔH and ΔS for the reaction were calculated to be 26 ± 2 kJ mol^{-1} and 1 ± 3 J mol^{-1} K^{-1} (298 K), respectively. The rate constant of the proton dissociation of the phenolic hydroxyl group in the complex AH was estimated to be *ca.* 2×10^5 s^{-1}.

In the course of a series of research works on the complexation reactions of metal ions with the multidentate ligands of triphenylmethane complexon[†††] type, Yamada discovered a phenomenon of thermochromism in the aqueous solution of copper(II)–XO complex.[1)] In the previous communication, we reported that the complexes of other triphenylmethane complexons with some bivalent metal ions are also thermochromic.[2)]

In the present paper, we report the thermochromism of the complexes of bivalent metal ions with various triphenylmethane complexons in aqueous media. We studied in detail the mechanism of the thermochromic change for the copper(II)–XO complex by means of the spectrophotometric and the temperature-jump method.

The mechanism was found to be quite different from that of the thermochromisms observed so far in the metal complexes in solutions, which were ascribed to the change in the configurational requirements on the central metal ions or the change in the ligand-field stabilization energies.[3,4)]

Experimental

Materials. All chemicals used were of analytical grade, unless otherwise specified. Water was deionized and distilled. Xylenol Orange was synthesized by Mannich condensation from *o*-Cresol Red, iminodiacetic acid (IDA), and formaldehyde.[5)] The crude sample of the synthesized XO was purified beforehand by means of cellulose column chromatography and finally by means of high-performance liquid chromatography.[6)] The purity of the specimen of XO was confirmed by elemental analyses and melting point measurements.[6)] Melting point was measured with a Rigaku Denki Differential Scanning Calorimeter Model 8001 SL/C. The purified XO was used as a free acid form. A 1.0×10^{-3} mol dm^{-3} stock solution of XO was prepared by dissolving a desired amount of XO in water.

The perchlorates of bivalent metals were prepared by heating the chlorides with small excess of perchloric acid until no trace of chloride ion was detected. The perchlorate was recrystallized from water. The stock solution was standardized titrimetrically with EDTA.

The pre-purified sodium perchlorate[7)] was heated in an oven at *ca.* 200 °C to prepare an anhydrous salt. A desired amount of the anhydrous perchlorate was dissolved in water to prepare a stock solution. Buffer solutions were prepared from 0.1 mol dm^{-3} acetic acid and 0.1 mol dm^{-3} sodium acetate.

Measurements. The equilibria were measured with Hitachi recording spectrophotometers Model EPS-3T and Model 323 equipped with a cell thermostated at high temperatures. A 1 cm quartz cell was used. The kinetic measurements were carried out with a Union Giken co-axial-cable temperature-jump apparatus Model RA-105.[8)] The pH values of the solutions were adjusted with acetate buffers and measured with a Hitachi-Horiba pH-meter Model F-7SS. For the pH measurements at high temperatures a glass electrode 1027-05T and a saturated calomel electrode 2631-05T were used. Temperature of the solution was measured with a copper-constantan thermocouple and a millivoltmeter. The ionic strength of the solution was adjusted to 0.1 mol dm^{-3} with sodium perchlorate.

Results and Discussion

Equilibria. In Table 1 are summarized the results of the thermochromism observed for the metal complexes of triphenylmethane complexons, which include both sulfonphthalein complexons and phthalein complexons. The structures and the abbreviated nomenclatures of the ligands are shown in Fig. 1(a) and Table 2. The results observed for the complexes of bivalent metal ions, Mg^{2+}, Ca^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}, were included in the table. Color changes of the aqueous solutions containing triphenylmethane complexons and 10—100 fold excess of metal ions have been studied at various buffered pH as a function of temperature by the measurements of visible absorption spectra as well as by visual observation. The thermochromic changes were observed only in the narrow pH range characteristic of the individual system.

The systems No. 1—29 in Table 1 include the com-

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[†††] Triphenylmethane complexons denote a series of multidentate ligands derived from the triphenylmethane dyes and iminodiacetic acid or other amino acids.

TABLE 1. THERMOCHROMISMS OF SOME METAL CHELATES WITH TRIPHENYLMETHANE COMPLEXONS a)

No.	Ligand	Metal ion	pH b) at 25 °C	Color (λ_{max}/nm c)) at room temperature	Color (λ_{max}/nm c)) at 60 °C	Remark d)
1	XO	Mg^{2+}	5.90	yellow (435)	reddish violet (575)	vs
2		Ca^{2+}	5.90	yellow (435)	reddish violet (580)	vs
3		Mn^{2+}	4.92	orange (440)	reddish violet (583)	vs
4		Co^{2+}	3.99	orange (452)	reddish violet (584)	s
5		Ni^{2+}	3.64	orange (452)	reddish violet (584)	s
6		Cu^{2+}	4.21	orange (450)	reddish violet (574)	vs
7		Zn^{2+}	3.97	orange (448)	reddish violet (572)	vs
8	MXB e)	Mg^{2+}	6.72	pale blue (450)	blue (606)	s
9		Ca^{2+}	5.90	green (440)	bluish green (590)	s
10		Mn^{2+}	5.04	yellow (446)	blue (615)	vs
11		Co^{2+}	3.81	pale yellow (468)	blue (618)	s
12		Ni^{2+}	3.80	yellow (456)	blue (618)	s
13		Cu^{2+}	4.34	yellow (460)	dark blue (600)	s
14		Zn^{2+}	4.06	dark yellow (464)	blue (610)	vs
15	MTB e)	Mg^{2+}	5.75	yellow (438)	yellow green (600)	s
16		Ca^{2+}	5.85	yellow green (438)	green (600)	s
17		Mn^{2+}	5.85	yellow (438)	green (605)	vs
18		Co^{2+}	3.67	yellow (460)	dark green (615)	vs
19		Ni^{2+}	3.67	yellow (446)	yellow green (618)	vs
20		Cu^{2+}	5.19	brown (444)	brown violet (600)	s
21		Zn^{2+}	3.80	yellow (454)	dark blue (598)	vs
22	CO f)	Cu^{2+}	4.38	orange (460)	pink (563)	s
23	GCR e)	Co^{2+}	5.24	dark yellow (438)	reddish violet (579)	s
24		Cu^{2+}	3.46	dark yellow (440)	reddish violet (576)	s
25	SCR g)	Co^{2+}	4.45	yellow (434)	reddish violet (578)	vs
26		Ni^{2+}	4.47	yellow (438)	reddish violet (578)	vs
27		Cu^{2+}	3.50	pale yellow (444)	reddish violet (572)	s
28		Zn^{2+}	4.82	yellow (444)	reddish violet (570)	vs
29	SXO g)	Cu^{2+}	5.46	orange (464)	reddish violet (570)	s
30	PC h)	Mg^{2+}	6.42	colorless (——)	violet (574)	vs
31		Mn^{2+}	5.27	pale violet (——)	violet (578)	vs
32		Ni^{2+}	4.82	colorless (——)	violet (580)	vs
33	PPC h)	Mg^{2+}	6.90	pale pink (——)	reddish violet (556)	vs
34	TPC h)	Mg^{2+}	7.11	colorless (——)	pale blue (608)	vs
35		Mn^{2+}	6.41	colorless (——)	blue (614)	s
36		Ni^{2+}	5.15	pale blue (——)	blue (618)	vs

a) Observed for the solutions containing $(1\text{—}5)\times10^{-5}$ mol dm^{-3} ligand and 10—100 fold excess of metal perchlorate. b) The pH, at which the remarkable thermochromic change was observed. Acetate buffer (CH_3COOH–CH_3COONa) and phosphate buffer (NaH_2PO_4–Na_2HPO_4) were used for the pH adjustment. c) λ_{max}'s represent the positions of the absorption maxima of the shorter- or the longer-wavelength absorptions. — denotes no, weak, or broad absorption. d) s: strong, vs: very strong. e) Purified by preparative thin-layer chromatography. See Ref. 9. f) Kindly supplied by Professor H. Nakayama, Kagawa Nutrition College. g) Purified by cellulose column chromatography. h) The commercial specimens of PC, PPC, and TPC (Dojindo, Kumamoto) were used.

TABLE 2. TRIPHENYLMETHANE COMPLEXONS LISTED IN TABLE 1 (See Fig. 1(a))

Ligand	R_1 a)	R_2 a)	R_3	R_4	R_5
Xylenol Orange (XO)	A	A	CH_3	H	SO_3H
Methylxylenol Blue (MXB)	A	A	CH_3	CH_3	SO_3H
Methylthymol Blue (MTB)	A	A	$CH(CH_3)_2$	CH_3	SO_3H
Cresol Orange (CO)	A	A	H	H	SO_3H
Glycine Cresol Red (GCR)	B	B	CH_3	H	SO_3H
Sarcosine Cresol Red (SCR)	C	C	CH_3	H	SO_3H
Semi-Xylenol Orange (SXO)	A	H	CH_3	H	SO_3H
Phthalein Complexon (PC)	A	A	CH_3	H	COOH
Phenolphthalein Complexon (PPC)	A	A	H	H	COOH
Thymolphthalein Complexon (TPC)	A	A	$CH(CH_3)_2$	CH_3	COOH

a) $A=CH_2N(CH_2COOH)_2$, $B=CH_2NHCH_2COOH$, $C=CH_2N(CH_3)CH_2COOH$.

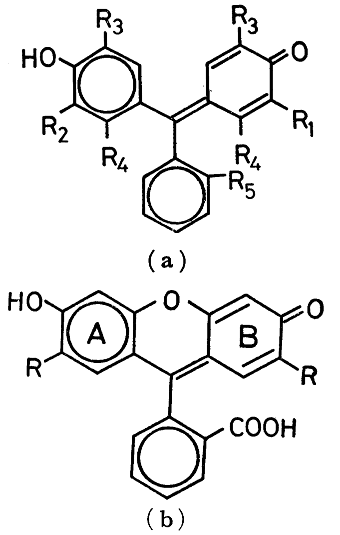

Fig. 1. The structures of the triphenylmethane complexons used. (a) Sulfonphthalein and phthalein complexons listed in Table 2. (b) Phthalein complexons with an ether linkage between two benzene rings. Calcein ($R=CH_2N(CH_2COOH)_2$) and Methyl Calcein ($R=CH_2N(CH_3)CH_2COOH$).

plexes of sulfonphthalein complexons. The absorption spectra of these complexes in visible region consist of two absorption bands. Temperature-dependencies of the spectra of these complexes were similar to the dependency shown in Fig. 2(a), *i.e.*, with a temperature-rise, the absorptions at longer wavelength increased, whereas those at the shorter wavelength decreased. The absorption spectra of the systems No. 30—36, which include the complexes of phthalein complexons, have only one absorption band in the visible region; The absorptions in the region 550—620 nm increased in intensities with a temperature-rise. The high-temperature color of the metal complexes of these one-color complexons strongly resembles the alkaline color of the corresponding parent phthalein dyes. The positions of the visible absorption bands suggest that the complexes responsible for the absorptions at high temperatures have a coordinated phenolate group. In order to clarify the mechanism of the thermochromism, the quantitative measurements have been carried out for the copper(II)–XO system.

It should particularly be emphasized that for the quantitative studies the use of the highly purified specimen of the ligand was essential. The use of commercial crude specimens of the triphenylmethane complexons, which are available only as metallochromic indicators or as colorimetric reagents, gave no definite quantitative results, though the qualitative observations of the thermochromic changes were still possible.

Figure 2(a) shows the visible absorption spectra at various temperatures of an aqueous solution containing 3.0×10^{-5} mol dm^{-3} XO and 1.2×10^{-4} mol dm^{-3} Cu^{2+} ion, the pH of the solution being adjusted at 3.94± 0.05. The most remarkable thermochromic change was observed in the pH region 3.8—4.5. In this pH region the solutions are orange at lower temperatures and reddish violet at higher temperatures. The absorption spectrum changes reversibly with a distinct isosbestic point at 491 nm, showing the existence of an equilibrium between two chemical species. As the temperature rises the absorbance at 450 nm decreases accompanied with a large increase in the absorbance at 574 nm. The absorbance at 574 nm increases about 4.5-fold for the temperature-rise from 7 to 78 °C.

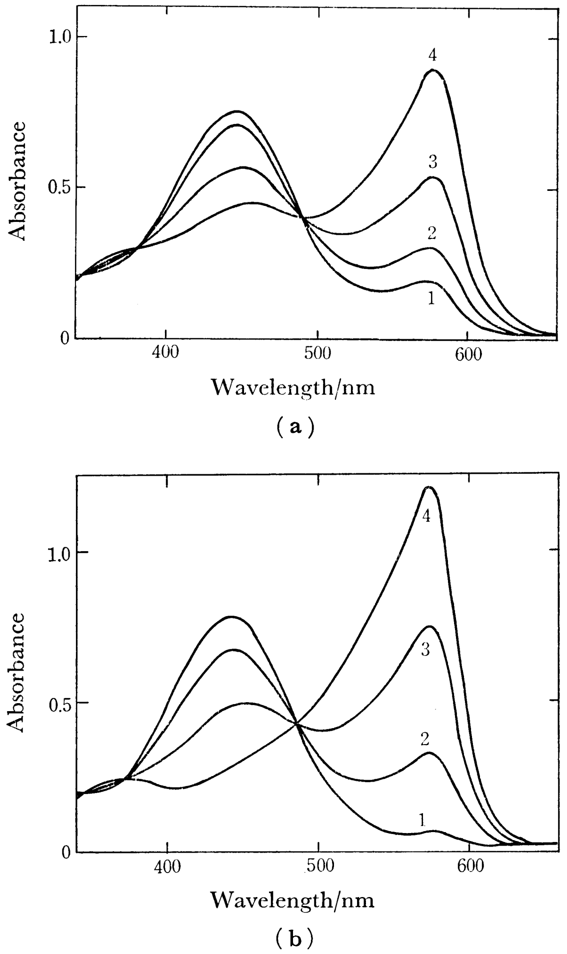

Fig. 2. Absorption spectra of the Cu(II)-XO. (a) Temperature-dependence. At 7 (1), 20 (2), 48 (3), and 78 °C (4). [Cu]$=1.2\times10^{-4}$ mol dm^{-3}; [XO]$=3.0\times10^{-5}$ mol dm^{-3}. $I=0.1$ mol dm^{-3} ($NaClO_4$). At pH=3.94±0.05. (b) pH-Dependence. At pH 2.99 (1), 3.93 (2), 4.49 (3), and 5.04 (4). [Cu]$=1.2\times10^{-4}$ mol dm^{-3}; [XO]$=3.0\times10^{-5}$ mol dm^{-3}. $I=0.1$ mol dm^{-3} ($NaClO_4$). At 25 °C. Cell length=1 cm.

Figure 3 shows the results of the molar-ratio method for the Cu(II)–XO complex measured at 574 nm, at various temperatures, and at pH 4.58±0.02. The metal-to-ligand ratio of the complex species formed in the solution was found to be invariably 2 : 1 irrespective of the temperature. For the solutions containing more than two-fold excess of Cu^{2+} ion over XO, the absorbance at a constant temperature increases only slightly even with the large increase in the concentration of Cu^{2+} ion, whereas for the solution at an arbitrary definite [Cu(II)] to [XO] ratio the absorbance increases markedly with the rise of temperature. This

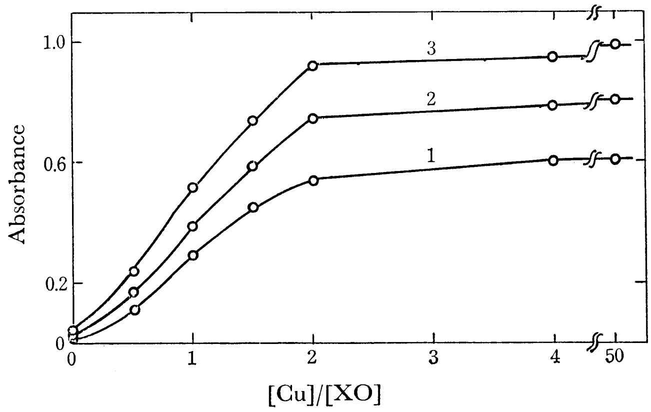

Fig. 3. Molar-ratio method at 574 nm for the Cu(II)-XO at various temperatures. At 25 (1), 50 (2), and 80 °C (3). $[XO]=3.0\times10^{-5}$ mol dm^{-3}. pH=4.58±0.02. $I=0.1$ mol dm^{-3} ($NaClO_4$). Cell length=1 cm.

fact indicates that the observed thermochromism should be ascribed to the temperature-dependence of an equilibrium between two 2 : 1 complex species, *i.e.*, between the low-temperature and the high-temperature form of a 2 : 1 complex species, but not to the step of complex formation between Cu^{2+} ion and the free ligand. In fact, the absorption maximum at the shorter wavelength observed in the presence of a large excess of Cu^{2+} ion ($\lambda_{max}=450$ nm) distictly differs from that of the free ligand in the given pH region ($\lambda_{max}=434$ nm).

The feature of the temperature-dependence of the absorption spectrum at a constant pH (Fig. 2(a)) was quite similar to that of the pH-dependence of the spectrum at a constnat temperature as depicted in Fig. 2(b). For the increase in the pH value of the solution from 3.93 to 5.04 the absorbance at 574 nm considerably increased about 3.7-fold accompanied with the corresponding decrease in the absorbance at 450 nm, and with a distinct isosbestic point at 491 nm. The observed wavelengths for the absorption maxima and the isosbestic point were found to be all the same as those for the temperature-dependence of the spectra at constant pH (Fig. 2(a)). It should be noted in this connection that the pH value of the acetate buffer solution used changed only slightly upon heating, *e.g.*, the solution of pH 4.55 at 20 °C shows the pH 4.62 even upon heating at 70 °C. The similarity of the temperature- and the pH-dependencies of absorption spectra suggests that the effect of heating of the solution essentially corresponds to the effect of the increase in pH of the same solution.

These facts indicate clearly that the observed thermochromism is primarily due to the temperature-dependence of the protolytic equilibria between the complex AH having an uncoordinated phenolic hydroxyl group and the complex A having a coordinated phenolate group

$$\underset{\text{(at lower temperatures)}}{AH} \quad \overset{K}{\rightleftharpoons} \quad \underset{\text{(at higher temperatures)}}{A + H.} \qquad (1)$$

The complex A is predominant at higher temperatures.

When the experiments were carried out in unbuffered aqueous solutions of the complex, the pH of the solution decreased with the rise of temperature. For example, if the pH of the solution containing 1.6×10^{-2} mol dm^{-3} $Cu(ClO_4)_2$ and 4.0×10^{-3} mol dm^{-3} XO ($I=0.1$ mol dm^{-3} ($NaClO_4$)) was adjusted at 4.53 at 25 °C only with $HClO_4$ and NaOH, the pH of the solution did decrease to 4.20 by heating the solution to 70 °C. The value of the pH at 70 °C accorded approximately with the calculated value of pK based on the ΔH and ΔS (see below). The same color change of the solution was observed as in the case of the buffered solution. These results directly confirm the dissociation of the proton from the species AH upon heating, which forms the hydrated proton in the unbuffered aqueous solution to lower the pH value of the solution as to be expected from the reaction mechanism (1).

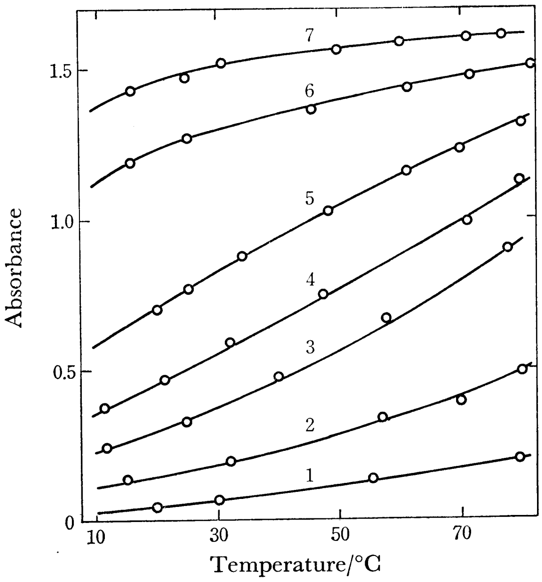

Fig. 4. The temperature-dependence of the absorbance at 574 nm of the Cu(II)-XO at various pH. At pH 2.99 (1), 3.53 (2), 3.94 (3), 4.21 (4), 4.49 (5), 5.04 (6), and 5.58 (7). $[Cu]=1.2\times10^{-4}$ mol dm^{-3}; $[XO]=3.0\times10^{-5}$ mol dm^{-3}. $I=0.1$ mol dm^{-3} ($NaClO_4$). Cell length=1 cm.

Figure 4 shows the temperature-dependence of the absorbance at 574 nm of the solution of the 2 : 1 Cu(II)-XO chelate at various buffered pH values. Upon heating the solution at pH higher than 5.0 or lower than 3.5 the absorbance increases only slightly. The largest increase in the absorbance was observed only in a narrow pH range between 3.9 and 4.5. This tendency suggests the existence of an optimum pH range for the given thermochromism. From the given temperature-dependence of the absorbance we can derive the pH-dependence of the absorbance at various temperatures as reproduced in Fig. 5. From the pH-dependences of the absorbance we calculated the values of pK for the equilibrium (1) at 15, 25, 35, 50, and 70 °C, which are listed in Table 3.

The uncomplexed free ligand XO did not show a thermochromic behavior at all around the pH region where its metal complexes are strongly thermochromic. However, in neutral or weakly basic media, *i.e.*, at

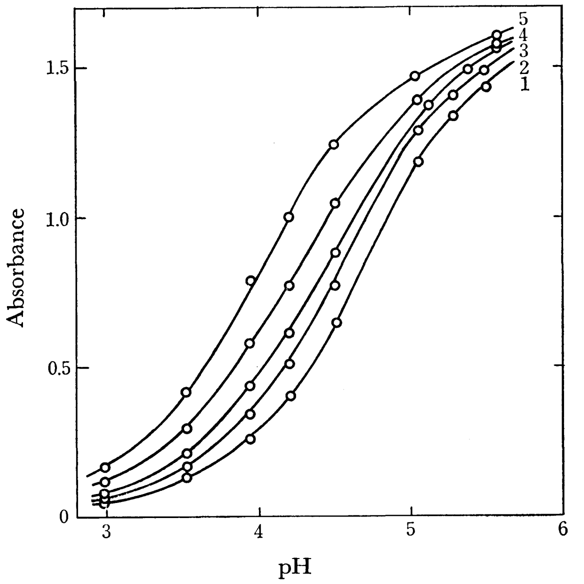

Fig. 5. The pH-dependence of the absorbance at 574 nm of the Cu(II)-XO at various temperatures. At 15 (1), 25 (2), 35 (3), 50 (4), and 70 °C (5). [Cu]=1.2×10^{-4} mol dm^{-3}; [XO]=3.0×10^{-5} mol dm^{-3}. I=0.1 mol dm^{-3} (NaClO$_4$). Cell length=1 cm.

TABLE 3. TEMPERATURE-DEPENDENCE OF THE ACID-DISSOCIATION CONSTANTS FOR THE Cu(II)-XO AND THE FREE XO AT I=0.1 mol dm^{-3} (NaClO$_4$)

Temperature °C	p(K/mol dm^{-3}) for Cu(II)-XO	p(K_a/mol dm^{-3}) for free XO
15	4.62	6.66
25	4.40, 4.55[a)]	6.57, 6.70[b)]
35	4.27	6.50
50	4.11	—
70	3.83	—

a) See Ref. 10. b) See Ref. 11.

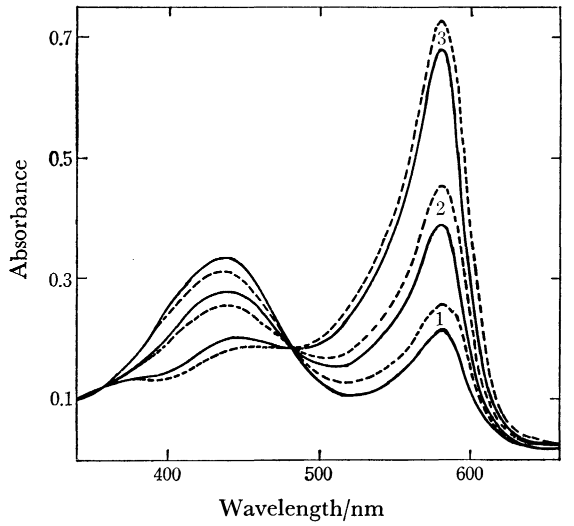

Fig. 6. Absorption spectra of the free ligand XO at various pH and temperatures. At pH 6.27 (1), 6.67 (2), and 7.14 (3). Temperature : 15 (—) and 35 °C (---). [XO]=3.0×10^{-5} mol dm^{-3}. I=0.1 mol dm^{-3} (NaClO$_4$). Cell length=1 cm.

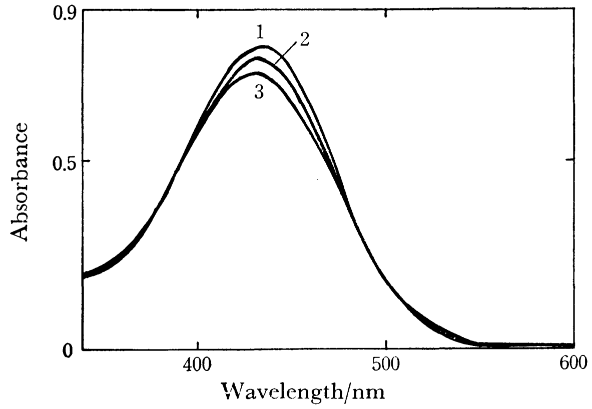

Fig. 7. Temperature-dependence of the absorption spectra of the free ligand XO at pH 3.47—3.97. [XO]=3.0×10^{-5} mol dm^{-3}. I=0.1 mol dm^{-3} (NaClO$_4$). At 6 (1), 25 (2), and 63 °C (3). Cell length=1 cm.

pH in the vicinity of the pK_a value of the phenolic proton, the free ligand XO were weakly thermochromic. Figure 6 shows the absorption spectra of the solution of the free ligand XO at two different temperatures and at three pH values. The temperature-dependence of the spectra was similar to the pH-dependence also in this case, the isosbestic point being identical in both cases. However, the thermochromic effect in the free ligand XO was much weaker compared with that in the Cu(II)-XO complex. Whereas upon heating from 15 to 35 °C the absorbance at 574 nm of a solution of the free ligand at pH 6.40, *viz.*, near the pK_a value of the phenol protons of the free ligand XO, increased only by 19%, the absorbance at 574 nm of the Cu(II)-XO system at pH 4.50 increased by so large as 36% for the same temperature-rise. The values of pK for the reaction $AH \rightleftharpoons A+H$ between two 2 : 1 Cu(II)-XO chelates decreases remarkably with the rise of temperature, whereas pK_a value of the phenol proton in the free ligand does not decrease so remarkably (Table 3).

The thermodynamic parameters ΔH and ΔS for the Reaction 1 and for the acid-dissociation of the phenol proton in the free ligand were graphically determined by plotting the values of $\log K$ and $\log K_a$ against $1/T$ to be 26±2 and 14±1 kJ mol^{-1} and 1±3 and -78 ± 1 J mol^{-1} K^{-1} (298 K), respectively. The positive values of the enthalpy show that the observed thermochromic changes are endothermic. The value of the enthalpy for the Cu(II)-XO complex is about twice as large as that for the free ligand. These results correspond to the fact that the more remarkable thermochromism is observed for reaction (1) than for the protolytic equilibrium of the free ligand. A small value of ΔS obtained for Eq. 1 would be due to the compensation of the increase in the entropy by a water molecule released from the coordination sphere of the metal ion upon coordination of the phenolate oxygen and the decrease in the entropy by the hydration of a dissociated proton. The values of ΔH and ΔS obtained for the free ligand are reasonable as the values for the usual proton-transfer reactions of the phenolic groups in aqueous media.[12)]

In addition, molar absorptivity of the free ligand XO were found to depend on the temperature. In the pH region between 3.47 and 3.97 corresponding to the pK_a of the carboxyl proton of the free ligand[11)] where the absorption spectra show no pH-dependency, the definite temperature-dependence of the spectra was clearly observed (see Fig. 7). This would be attributed to the change in molar absorptivity of the free ligand. Therefore, the temperature-dependency of the molar absorptivity might also contribute to the thermochromic behavior of the present complexes, though the effect is not so strong.

It is interesting to note that the metal complexes of the triphenylmethane complexons with the two benzene rings A and B tightly linked together, say, *e.g.*, through an ether linkage as shown in Fig. 1(b), were not thermochromic. This fact shows the possibility that the change in resonance structure of the π-system of the triphenylmethane skeleton could also contribute to the thermochromic changes.

Kinetics. The temperature-jump studies were carried out for the thermochromic changes of the Cu(II)-XO complex together with the Co(II), Ni(II), and Zn(II) complexes of XO, and also for the acid-dissociation of the free ligand in the pH range where the thermochromic changes were observed. The relaxation times τ observed in 5 μs region can be expressed as

$$\tau^{-1} = k_1 + k_{-1}([\overline{\mathrm{H}}]+[\overline{\mathrm{A}}]). \tag{2}$$

As regards the acid-dissociation of phenolic proton in the free ligand in aqueous media, we obtained the values of the rate constants for the deprotonation and for the protonation $k_1=(1.0\pm0.6)\times10^4\ \mathrm{s^{-1}}$ and $k_{-1}=(3.0\pm0.1)\times10^{10}\ \mathrm{mol^{-1}\,dm^3\,s^{-1}}$, respectively (Fig. 8). The value of k_1 lies in the same order of magnitude as the values of the rate constants reported for the acid-dissociation of the phenolic ligands of similar structure[13)] and the quotient $k_1/k_{-1}=10^{-6.5}\ \mathrm{mol\,dm^{-3}}$ is in good agreement with the acid-dissociation constant, K_a, of the phenolic proton of XO.[11)] However, from the signals of the temperature-jump observed for the thermochromic changes of the metal chelates we could evaluate only the approximate values of the rate constants for reaction (1), since the values of τ as derived from the exponential signals (see Table 4) lie just near the time constant τ_c for the temperature-rise of our apparatus. The value of k_1 estimated for reaction (1) was *ca.* $2\times10^5\ \mathrm{s^{-1}}$. Similar temperature-jump studies were also carried out preliminarily for the Co(II)-XO, Ni(II)-XO, and Zn(II)-XO systems. The corresponding k_1 values for these systems were found to be *ca.* $2\times10^5\ \mathrm{s^{-1}}$, essentially independent of the metal ion involved. Thus the kinetic measurements also suggest that the phenomena of the thermochromism observed in the presence of a large excess of metal ions are primarily due to the process involving a protonation-deprotonation in the coordinated ligand. The quantitative studies for other thermochromic systems are now in progress and will be reported elsewhere.

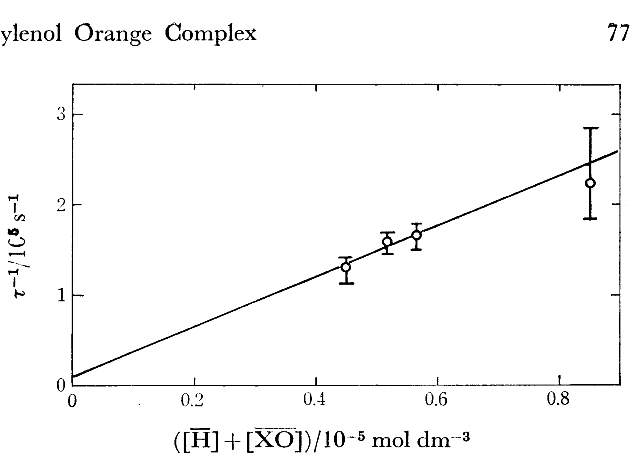

Fig. 8. Plot of τ^{-1} *vs.* $([\overline{\mathrm{H}}]+[\overline{\mathrm{XO}}])$ at 25 °C for the acid-dissociation of the free ligand XO. $[\mathrm{XO}]=3.0\times10^{-5}\ \mathrm{mol\,dm^{-3}}$. $I=0.1\ \mathrm{mol\,dm^{-3}}$ ($\mathrm{NaClO_4}$).

Table 4. The reciprocal of the relaxation times for the deprotonation-protonation of the $\mathrm{Cu_2(XO)}$, $\mathrm{AH \rightleftharpoons A+H}$ at 25 °C and $I=0.1\ \mathrm{mol\,dm^{-3}}$ ($\mathrm{NaClO_4}$)

$[\overline{\mathrm{A}}]+[\overline{\mathrm{H}}]$ / 10^{-4} mol dm^{-3}	τ^{-1} / 10^5 s^{-1}
0.32	2.8
0.37	2.6
0.70	2.7
1.28	2.9
1.33	2.4

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