

Photoreactivity and Thermogravimetry of Copper(II) Complexes of *N*-Salicylideneaniline and Its Derivatives

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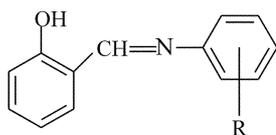
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Cu^{II}-complexes of *N*-salicylideneaniline and its derivatives were not light sensitive in most solvents such as acetonitrile. A photo-decomposition occurred upon irradiation in halocarbon solvents such as CHCl₃. It has been suggested that such photoreactivity is attributed to the reactivity of charge-transfer to solvent (CTTS) excited state attained upon irradiation. A mechanism has been proposed to account for the results obtained. The complexes have been thermally analysed in nitrogen and static air using thermogravimetry (TG) and derivative thermogravimetry (DTG). The thermal degradation of the complexes proceeds in two or three stages. The kinetic parameters obtained from the Coats-Redfern and Horowitz-Metzger equations show the kinetic compensation effect.

Key Words : Cu^{II}-complexes of *N*-salicylideneaniline, Charge transfer to solvent (CTTS), Photochemistry, Thermogravimetry

Introduction

Schiff bases form stable complexes with metals that perform important role in biological systems.¹ They find also wide applications in analytical chemistry since they allow simple and inexpensive determinations of several organic and inorganic substances. Furthermore, many Schiff bases exhibit antiviral and antibacterial activity and can also be regarded as mimetic systems for enzyme models.^{2,3} Some Schiff base complexes were found to be very effective catalysts for hydrolytic cleavage or transesterification of RNA phosphate diester backbone.⁴ Therefore metal complexes of Schiff bases attained a prominent place in coordination chemistry, which was shown over many years by the large number of publications⁵ and by the comprehensive reviews.^{6,7} In view of the above mentioned importance of Schiff bases and their complexes and due to the fact that few reports are known in the literature regarding photochemical⁸ and thermal behaviour⁹⁻¹¹ of Schiff base complexes, we performed photolysis and thermogravimetric studies on Cu^{II}-complexes of *N*-salicylideneaniline and its derivatives (I) as a continuation of our previous interest in this respect.¹²⁻¹⁴



R = H, o-OCH₃, o-CH₃ or p-CH₃

(I)

Experimental Section

Materials. All chemicals were of analytical grade. The Cu^{II} complexes, bis(*N*-salicylideneaniline)copper(II), [Cu(SA)₂]; bis(*N*-salicylideneaniline)(dichloro)copper(II) dihydrate, [Cu(SA)₂Cl₂]·2H₂O; bis(*N*-salicylidene-*o*-anisidine)copper(II), [Cu(SOA)₂]; bis(*N*-salicylidene-*o*-toluidine)copper(II), [Cu(SOT)₂] and bis(salicylidene-*p*-toluidine)copper(II), [Cu(SPT)₂] were prepared according to literature procedures.¹⁵

Photolyses. The light source was an Osram HBO 200 W/2 Lamp. Monochromatic light was obtained using the Scholt IL interference filter 298 nm. The photolyses were carried out in solutions of different solvents in 1 cm spectrophotometer cells at room temperature. Progress of the photolyses was monitored by using a UV-2101 PC shimadzu spectrophotometer. For quantum yield determinations the complex concentrations (~10⁻² M) were chosen so as to attain a complete light absorption. Absorbed light intensities were determined by ferrioxalate actinometry.¹⁶ The photoproducts were identified by their absorption spectra. The absorptions at the maxima of 330-350 nm were used to determine the concentration of the photoproducts (the free ligands) after subtracting the absorbance of the starting complexes. It is to be noted that the photolyses in the presence of air and in deaerated solutions (nitrogen atmosphere) are the same indicating that oxygen has no effect.

Thermogravimetric analyses. Shimadzu TGA-50 H thermal analyser was used for recording thermogravimetric data of the complexes in a dynamic nitrogen atmosphere (20 mL min⁻¹) at a heating rate of 10 °C min⁻¹. In static air the measurements were achieved using an electrobalance of the Sartorius 200 MP type, converted to a thermobalance by inclusion of a small furnace and sample holder. The temperature was monitored using a Chromel-Alumel thermocouple

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attached to a digital multimeter type Soar ME-550. The heating rate was adjusted to $8\text{ }^{\circ}\text{C min}^{-1}$.

Results and Discussion

Photochemical behaviour. Upon irradiating solutions of the studied Cu^{II} -complexes with light of wavelength 298 nm in solvents like ethanol, acetonitrile or DMF no spectral changes were recorded at different irradiating intervals. On the other hand, these complexes undergo a photochemical reaction in halocarbon solvents such as CH_2Cl_2 , CHCl_3 and CCl_4 . The spectral changes recorded during photolysis ($\lambda_{\text{irr}} = 298\text{ nm}$) of $[\text{Cu}(\text{SPT})_2]$ in CCl_4 as an typical example are given in Figure 1. The reaction is rather clean as indicated by sharp isosbestic points at $\lambda = 316$ and 368 nm . The spectral changes associated with photolysis show that the longer wavelength band due to the Cu^{II} -complex gradually disappears while a new band due to the free ligand appears. At the end of photolysis the spectrum of the photolyzed solution nearly coincides with that of the free ligand.

These results indicate that the photolysis leads to decomposition of complexes and release of free ligands. It has been suggested that the observed photochemical reaction is a result of a photooxidation step as a key step. By analogy^{17,18} with other photooxidations in halocarbon solvents, where solvent molecules act as electron acceptors, the following mechanism could be suggested to account for our results:

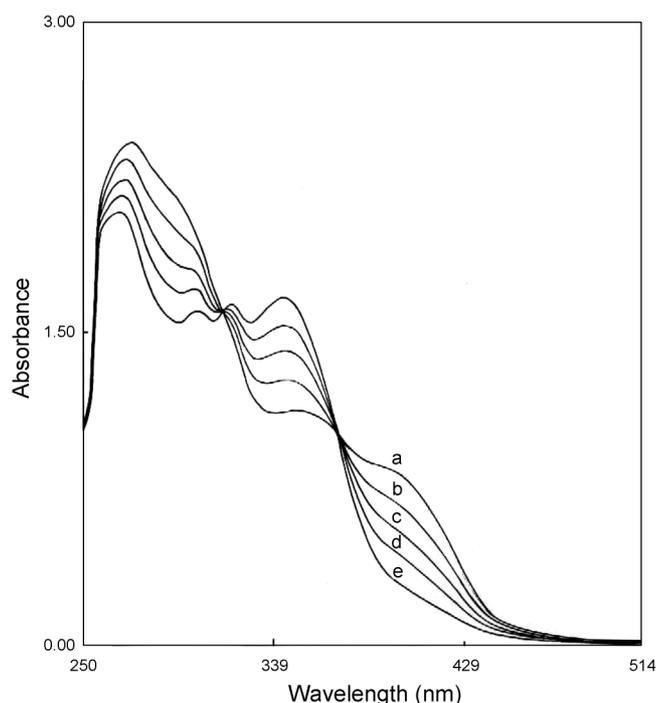
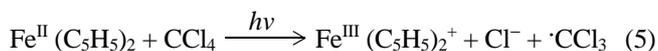


Figure 1. Spectra changes during the photolysis of $[\text{Cu}(\text{SPT})_2]$ in CCl_4 . Irradiation time: (a) 0, (b) 40, (c) 80, (d) 160, (e) 320 sec. ($\lambda_{\text{irr}} = 298\text{ nm}$; 1 cm cell).



Absorption of irradiating light leads to formation of a charge-transfer-to-solvent (CTTS) excited state, in which the starting complex transfers an electron to CHCl_3 in a primary photochemical step (reaction 1). The resulting complex cation is apparently not stable and decomposes to CuL^+ and $\cdot\text{L}$ in a secondary step (reaction 2). The formed Cl^- , $\cdot\text{CHCl}_2$ and CuL^+ may react to regenerate the neutral CuL and solvent molecule. Two of $\cdot\text{L}$ may dimerize giving a compound of a related spectrum to the free ligand.

The CTTS excited state can be reached by direct absorption into a CTTS band or by internal conversion from the other excited states. In the present study the presence of a CTTS band was not detected, since such a low intensity band may be obscured by the intense intramolecular absorption of the complexes.¹⁹ Irrespective of the presence of CTTS bands, most of light causing photooxidation of the complexes under investigation is certainly absorbed by bands of a different origin. Such conclusion was also adopted in the photooxidation of 1,2-dithiolene complexes of Ni^{II} , Pd^{II} and Pt^{II} in chloroform.¹⁸ Furthermore, distinct CTTS absorptions appear in the electronic spectra of certain organometallic complexes in halocarbon solvents.^{19,20} For example, ferrocene shows a new absorption at $\lambda_{\text{max}} = 307\text{ nm}$ if it is dissolved in CCl_4 ^{21,22} and this band was assigned to a CTTS transition. Upon excitation, ferrocene was photo-oxidized.^{20,23} The primary photochemical step proceeds according to equation 5:



For our complexes, the energy of the CTTS state depends on the redox potential of the solvent. The quantum yield ($\lambda_{\text{irr}} = 300\text{ nm}$) of photo-oxidation was determined in CH_2Cl_2 ($E = -2.33\text{ V vs. SCE}$),²⁴ in CHCl_3 ($E = -1.67\text{ V}$)²⁴ and in CCl_4 ($E = -0.78\text{ V}$).²⁴ It seems that the quantum yield of the photooxidation increases with increasing the oxidation power of the solvent (Table 1). This behavior is characteristic of the reactivity of CTTS excited states. Such conclusion has been also reported for the photooxidation of bis(ethylxanthato)nickel(II) containing aromatic nitrogen heterocyclic ligands in CHCl_3 .¹⁷

A further evidence supports the proposed photooxidation

Table 1. Photolysis quantum yields (Φ) of Cu^{II} -complexes in halocarbon solvents

Complex	Φ		
	CH_2Cl_2	CHCl_3	CCl_4
$[\text{Cu}(\text{SA})_2]$	0.009	0.029	0.38
$[\text{Cu}(\text{SA})_2\text{Cl}_2] \cdot 2\text{H}_2\text{O}$	0.008	0.025	0.33
$[\text{Cu}(\text{SOA})_2]$	0.007	0.030	0.35
$[\text{Cu}(\text{SOT})_2]$	0.008	0.031	0.29
$[\text{Cu}(\text{SPT})_2]$	0.006	0.028	0.30

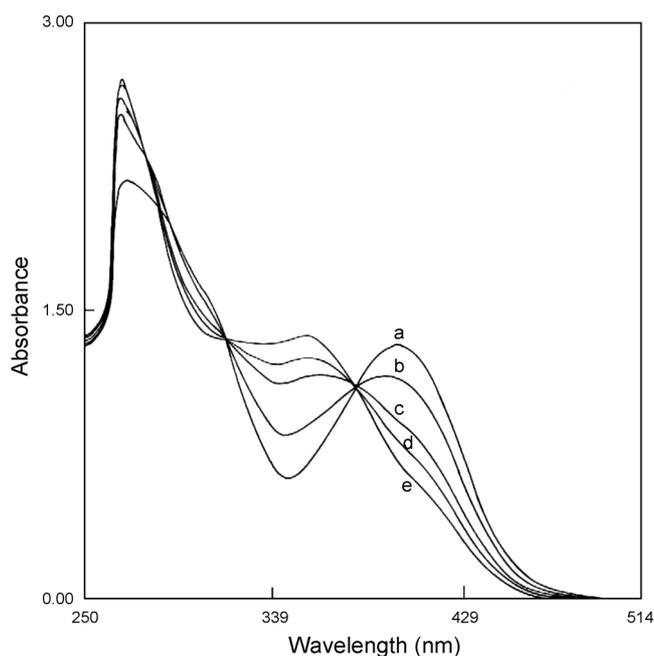
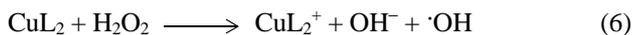
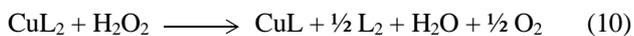


Figure 2. Spectral changes recorded upon adding some drops of H_2O_2 to DMF solution of $[\text{Cu}(\text{SOT})_2]$ after (a) 1, (b) 2, (c) 4, (e) 8 min. of mixing.

mechanism can be formulated as follows. Upon adding some drops of H_2O_2 to DMF solutions of Cu^{II} -complexes (which are photostable under the studied conditions) similar spectral changes to those obtained upon irradiation in halocarbon solvents were recorded (Figure 2 as a representative example). The final products were identified from the spectrum to be also the free ligands of the corresponding Cu^{II} -Schiff base complexes. The following mechanism is proposed to account for the results obtained:



The overall reaction is



It is to be noted that solutions of the free ligands under investigation in halocarbon solvents are photoinactive upon irradiation with light of $\lambda_{\text{irr}} = 298$ nm. Also no spectral changes were observed upon addition of few drops of H_2O_2 to the DMF solution of the free ligands. This is not surprising, since the oxidation of coordinated ligand is so easy than that of the free one.²⁵

It is thus concluded that although the photolysis of the studied Cu^{II} complexes leads to no net redox products, however, certainly the primary photochemical step (reaction 1) is a redox process. This can be supported by the following considerations (i) the photoreaction occurs only in halocarbon solvents, which are known as electron acceptors

Table 2. Thermal data of Cu^{II} -complexes in nitrogen atmosphere and static air^a

Complex	Nitrogen Flow			Static Air				
	Step	T_i	T_m	T_f	Step	T_i	T_m	T_f
$[\text{Cu}(\text{SA})_2]$	1st	145	200	260	1st	140	210	255
	2nd	265	325	400	2nd	260	320	360
$[\text{Cu}(\text{SA})_2\text{Cl}_2] \cdot 2\text{H}_2\text{O}$	1st	100	197	250	1st	90	160	200
	2nd	255	307	375	2nd	240	333	365
	3rd	455	517	580	3rd	440	533	570
$[\text{Cu}(\text{SOA})_2]$	1st	210	281	350	1st	205	300	340
	2nd	360	383	448	2st	345	375	400
	3rd	448	510	630	3rd	400	450	500
$[\text{Cu}(\text{SOT})_2]$	1st	254	291	230	1st	215	297	350
					2nd	320	448	490
					3rd	490	500	520
$[\text{Cu}(\text{SPT})_2]$	1st	125	321	383	1st	120	300	385
	2nd	383	450	550	2nd	385	493	590
					3rd	590	595	650

^a T_i = initial temperature; T_m = temperature at the DTG peak; T_f = final temperature

(ii) the quantum yield of the photooxidation depends on the redox potential of the solvent (iii) the DMF solutions of the complexes, which are photoinactive give the same spectral changes as that of the photolysis upon treatment with some drops of H_2O_2 .

Thermal behaviour. The thermal behaviour of the copper (II) complexes of *N*-salicylideneaniline and its derivatives was studied in nitrogen and static air atmospheres using thermogravimetric (TG) and derivative thermogravimetric (DTG) techniques. Table 2 lists the initial, maximum and final temperatures of the different decomposition steps.

The thermolysis curve of $[\text{Cu}(\text{SA})_2]$ in nitrogen atmosphere (Figure 3) exhibits two decomposition steps at 200 and 325 °C (DTG curve). The first step is a small step (4.8%) while the second one is a major step representing a mass loss of 55.2% and activation energy of 49.0 kJ/mol. Two decomposition steps were also recorded in static air at 210 and 320 °C (DTG). The first step is a small step (4.4%) whereas the second step (major step) is accompanied by a

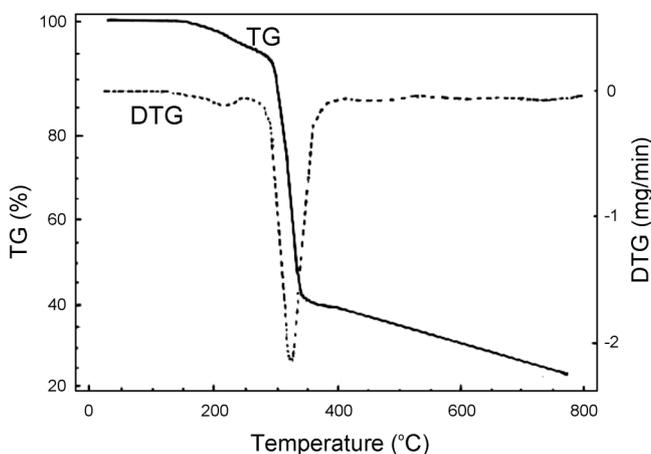


Figure 3. TG-DTG curves of $[\text{Cu}(\text{SA})_2]$.

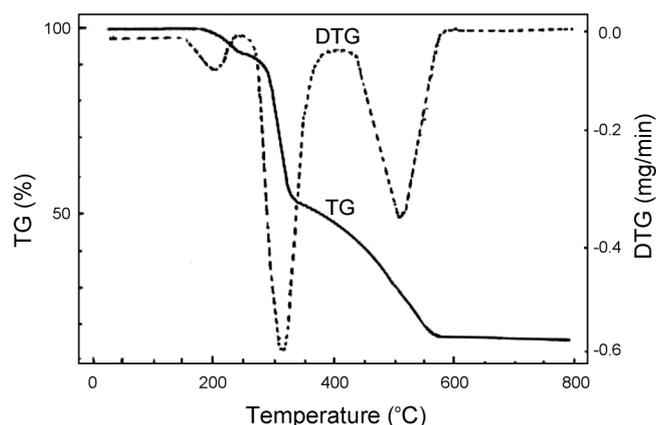


Figure 4. TG-DTG curves of $[\text{Cu}(\text{SA})_2\text{Cl}_2]\cdot 2\text{H}_2\text{O}$.

55.2% mass loss. As a final product CuO is obtained (calc. 17.4%, found 18.0%).

The TG curve of $[\text{Cu}(\text{SA})_2\text{Cl}_2]\cdot 2\text{H}_2\text{O}$ in nitrogen flow (Figure 4) indicates that the complex decomposes in three decomposition stages at 197, 307 and 517 °C (DTG). The first step seems to be consistent with the evolution of two water molecules (calc. 6.3%, found 6.5%) with an activation energy of 101.0 kJ/mol (Coats-Redfern). The ligand decomposes in the two subsequent steps with the formation of CuO as a final residue (calc. 14.0%, found 14.5%). In static air three decomposition stages at almost the same TG peaks as in nitrogen atmosphere, namely at 160, 333 and 533 °C were observed; CuO is the end product (calc. 14.1%, found 15.0%).

The pyrolysis curve of $[\text{Cu}(\text{SOA})_2]$ in nitrogen atmosphere (Figure 5) involves three steps at 281, 383 and 510 °C (DTG). In static air the complex, however, displays three steps at 300, 375 and 450 °C. In nitrogen flow as well as in static air the first step is commensurate with the elimination of two methoxybenzene radicals (calc. 41.7%, found 41.5%). The end mass loss in static air indicates the formation of CuO in good agreement with the calculated value (calc. 15.4%, found 15.0%).

The TG curve of $[\text{Cu}(\text{SOT})_2]$ in nitrogen atmosphere (Figure 6) yields a major step (49.5%), indicated on the

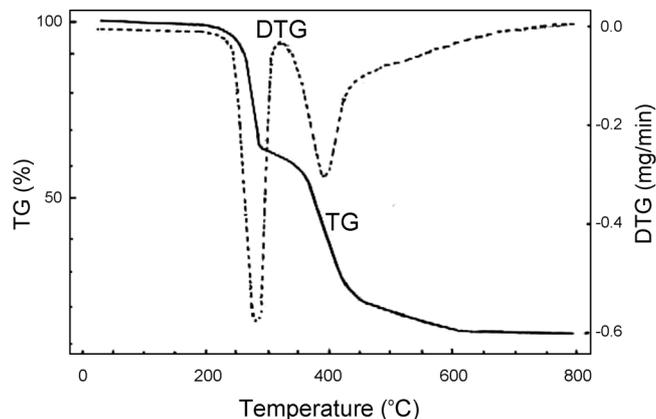


Figure 5. TG-DTG curves of $[\text{Cu}(\text{SOA})_2]$.

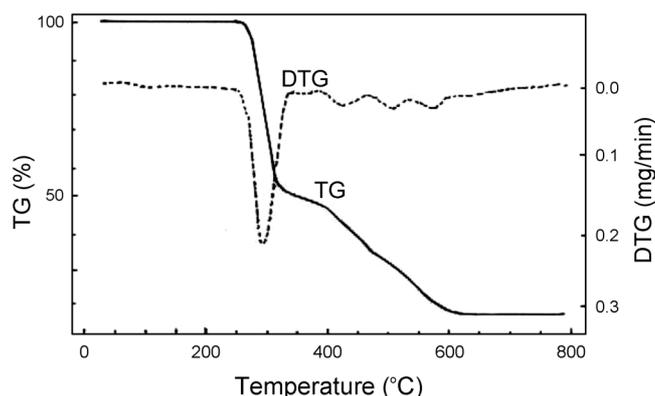


Figure 6. TG-DTG curves of $[\text{Cu}(\text{SOT})_2]$.

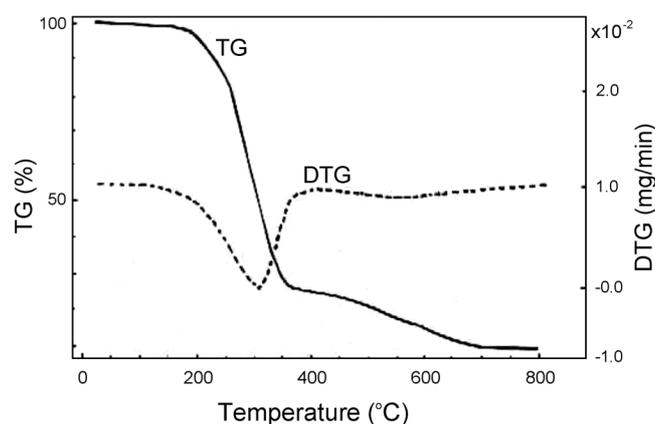
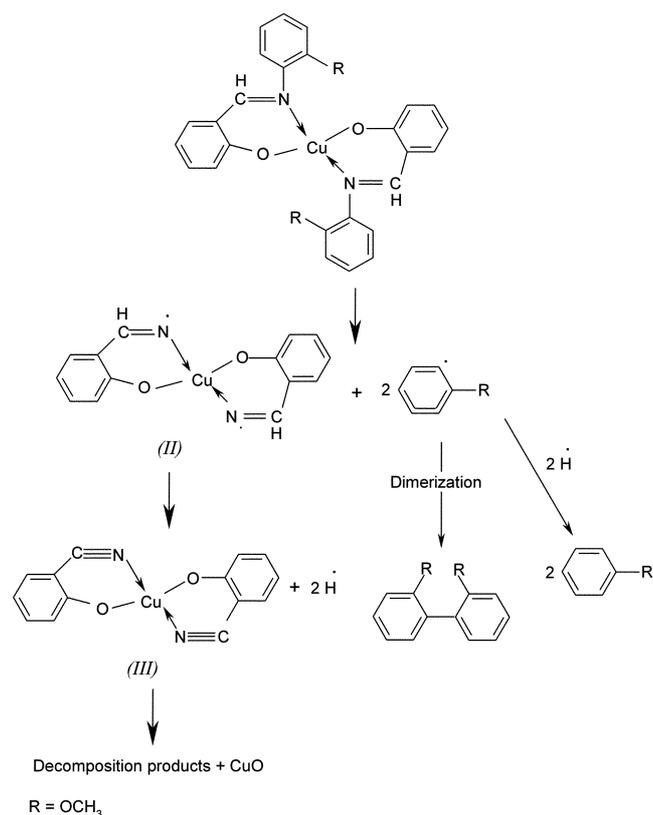


Figure 7. TG-DTG curves of $[\text{Cu}(\text{SPT})_2]$.

DTG curve at 291 °C. Thereafter a mass loss continues in a relatively long downhill step until a species attains a constant mass at 750 °C, which corresponds to the formation of CuO. In static air three steps at 297, 448 and 500 °C are observed, the first step is a major step. The final residue is CuO (calc. 16.4%, found 17.0%).

In its TG thermogram in nitrogen atmosphere $[\text{Cu}(\text{SPT})_2]$ exhibits two decomposition stages indicated on the DTG curve at 321 and 450 °C (Figure 7). Afterwards a continuous decomposition sets in until 700 °C. The first is accompanied by a mass loss of 72.5% (activation energy of 43 kJ/mol). The mass loss of the second step amounts to 9.8%. However, three steps are noticed in static air. The first step of 66.6% occurs at 300 °C and the value of its activation energy amount to 36.0 kJ/mol. The second and third steps are indicated on the TG and DTG curves at 493 and 595 °C, respectively. The final product consists of CuO (calc. 14.0%, found 15%).

A suggested decomposition mechanism of $[\text{Cu}(\text{SOA})_2]$ (and probably for the other complexes) is given in Scheme 1. The first step of the two TG curves in nitrogen and static air represents a mass loss corresponding to the expulsion of two methoxyphenyl radicals leaving the complex radical(II). The latter loses hydrogen to give the Cu^{II} -nitrile complex(III) while the methoxybenzene radical may abstract hydrogen to afford a methoxybenzene molecule or dimerize to give the

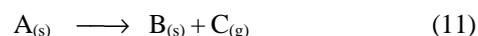
**Scheme 1.** Thermal decomposition mechanism of [Cu(SOA)₂].

diphenyl derivative. The nitrile complex decomposes in the subsequent steps to give CuO as a final product.

Formation of nitrile intermediates during the thermal decomposition of Schiff bases was previously reported for

some aromatic Schiff bases.²⁶

Kinetic analyses. Non-isothermal decomposition of the metal complexes under study resembles the reaction



which can be studied kinetically. The kinetic studies were carried out making use of two different procedures: the Coats-Redfern²⁷ and the Horowitz-Metzger²⁸ methods. Table 3 includes the kinetic parameters, reaction order (n), activation energy (E), pre-exponential factor (Z) and entropy of activation (ΔS) together with the correlation coefficient (r). These parameters were evaluated only for clear-cut and non-overlapping stages. Kinetic studies were not attempted for decomposition stages, which occur within a very narrow temperature range, resulting in a TG curve too steep for enough data to be collected.

The calculated activation energies of the complexes are relatively low indicating the autocatalytic effect of copper on the thermal decomposition of the complexes. Catalytic activity of many catalysts containing Cu(II) was reported in the literature.^{29,30} The negative values of ΔS for most of the complexes means that the activated complex is more ordered than the reactant and that the reactions are slow. The more ordered nature may be due to polarization of bonds in the activation state, which might happen through charge transfer electronic transitions.

Kinetic compensation effect. The effect of sample weight on the TG curves of [Cu(SOA)₂] and [Cu(SOT)₂] was studied. The TG curves exhibit a shift towards higher temperature by increasing sample weight. The concept of the so called kinetic compensation effect, which was observed in many non-isothermal processes,^{31,32} is seen to be valid here.

Table 3. The kinetic parameters of Cu^{II}-complexes^a

Complex	Coats-Red. Eq.						Horowitz eq.				
	Step	n	r	E	Z	ΔS	(I) Nitrogen flow				
							n	r	E	Z	ΔS
[Cu(SA) ₂]	1st	2.0	0.9867	190	3.82×10^{13}	11	2.0	0.9925	204	5.67×10^{14}	33
	2nd	2.0	0.9831	49	1.97×10^4	-165	2.0	0.9961	67	7.71×10^4	-154
[Cu(SA) ₂ Cl ₂]-2H ₂ O	1st	1.0	0.9978	101	6.54×10^8	-79	1.0	0.9998	107	2.49×10^9	-68
	2nd	0.66	0.9980	127	8.10×10^8	-79	0.66	0.9968	131	8.77×10^9	-60
	3rd	2.0	0.9882	224	4.51×10^{12}	-10	2.0	0.9981	218	6.18×10^{11}	-27
[Cu(SOA) ₂]	1st	0.0	0.9975	61	1.56×10^3	-188	0.0	0.9990	66	2.66×10^3	-184
	2nd	0.66	0.9951	98	2.50×10^6	-128	0.66	0.9988	111	2.55×10^7	-109
[Cu(SOT) ₂]	1st	2.0	0.9981	198	3.82×10^{14}	-156	2.0	0.9911	199	2.88×10^{15}	-155
[Cu(SPT) ₂]	1st	0.66	0.9954	43	7.94×10^4	28	0.66	0.9955	49	3.45×10^4	45
							(II) Static air				
[Cu(SA) ₂]	2nd	0.33	0.9952	37	5.83×10^5	-140	0.33	0.9929	39	5.23×10^4	-160
[Cu(SA) ₂ Cl ₂]-2H ₂ O	1st	1.0	0.9962	97	3.00×10^9	-66	1.0	0.9966	113	2.56×10^{10}	-48
	2nd	1.0	0.9879	120	1.30×10^9	-76	1.0	0.9886	130	9.84×10^{10}	-40
	3rd	0.66	0.9964	224	3.01×10^{12}	-14	0.66	0.9901	215	1.38×10^{12}	-20
[Cu(SOA) ₂]	1st	0.33	0.9893	51	6.37×10^3	-177	0.33	0.9973	55	4.35×10^4	-161
	2nd	0.5	0.9858	84	8.60×10^4	-156	0.50	0.9954	89	4.11×10^5	-143
[Cu(SOT) ₂]	1st	1.0	0.9844	149	6.05×10^{10}	-163	1.0	0.9936	156	3.21×10^{11}	-141
[Cu(SPT) ₂]	1st	0.66	0.9905	36	3.31×10^4	-43	0.66	0.9961	41	4.72×10^5	-30

^aE in kJ mol⁻¹, Z in S⁻¹, ΔS in JK⁻¹mol⁻¹

It was reported that for a particular process the value of E bears a definite linear relationship to $\ln Z$, viz.

$$\ln Z = a E + b \quad (12)$$

Where a and b are constants. The equation to this straight line, as obtained by linear squares method for the above two complexes is written as follows:

i) for $[\text{Cu}(\text{SOA})_2]$

$$\ln Z = 0.23 E - 11.40 \quad (13)$$

ii) for $[\text{Cu}(\text{SOT})_2]$

$$\ln Z = 0.19 E + 9.50 \quad (14)$$

Garn^{33, 34} defined a "characteristic temperature T_c " which is related to the slope (a) of the straight-line plot according to:

$$T_c = 1/Ra \quad (15)$$

The physical significance of T_c is, however, not very clear. For each of the above two complexes, the value of T_c was calculated and it was found that the two values of T_c fall within the experimental temperature range, namely 593 K for $\text{Cu}(\text{SOA})_2$ and 512 K for $\text{Cu}(\text{SOT})_2$, so the kinetic compensation effect holds good for the non-isothermal decomposition of the two complexes.

Finally, the following conclusion remarks can be summarized:

(i) The thermal decomposition of the complexes occurs in two or three stages.

(ii) The autocatalytic effect of copper on the thermal decomposition of the complexes is apparent and the activation energies of decomposition are relatively low. (iii) The kinetic parameters show the kinetic compensation effect and the correlation between activation energy (E) and natural logarithm of pre-exponential factor ($\ln Z$) is of a linear nature. This may indicate the influence of change in sample mass on the estimated values of activation energy and pre-exponential factor. (iv) The courses of the decomposition steps are generally different in both nitrogen and static air atmospheres.

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