

## Kinetics, Mechanism & Synthetic Applications of Thermal Decomposition of Cu(II) Chelates of Acetoacetanilide & $\alpha$ -Chloroacetoacetanilide

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Considerable difference has been observed in the thermal decompositions of Cu(II) chelates of acetoacetanilide, and  $\alpha$ -chloroacetoacetanilide. This difference has been explained on the basis of intramolecular N-H...Cl hydrogen bonding present in the latter complex. Both the intermediate and final products of thermal decomposition have been identified, and are in agreement with the proposed mode of decomposition. Controlled pyrolysis of Cu(II) chelates of acetoacetanilides has been found to be an excellent method for preparing the corresponding phenyl isocyanates. Kinetic study has revealed that Mampel, and Avrami equations govern respectively the rates of decomposition of acetoacetanilide and  $\alpha$ -chloroacetoacetanilide chelates.

HERMAL analysis has been used to study the stability of metal complexes<sup>1</sup>. However, kinetics and mechanism of only a few of the solid state reactions have been investigated<sup>2,3</sup>. Direct correlation between thermal and solution stabilities was not observed for certain very stable metal chelates, presumably because their decomposition did not commence with the scission of the metal-ligand bond(s)<sup>4,5</sup>. Although thermal studies can reveal the differences in strengths of metal-ligand bonds of unsymmetrically constituted chelating ligands, no such study has been reported. An attractive aspect of thermogravimetry, namely its synthetic advantage, remains unexploited for metal chelates. The present study is an attempt to examine all these aspects for Cu(II) chelates of acetoacetanilide and  $\alpha$ -chloroacetoacetanilide.

In our earlier studies on metal chelates of variously substituted acetoacetanilides, we found that although stability in general decreased with increasing electron-withdrawing character of the substituent, the acetoacetanilides containing a halogen on the  $\alpha$ -carbon behaved anomalously<sup>6</sup>. Intramolecular hydrogen bonding between the NH hydrogen and the  $\alpha$ -halogen seemed responsible for this abnormal behaviour. Unless held by the hydrogen bond, the NH hydrogen (structure I) would migrate tautomericly to the amide oxygen

(amide resonance would facilitate this transfer<sup>7</sup>) thus weakening the amide oxygen-metal bond. Since chelate resonance is expected to be weak, the two metal-oxygen bonds of the same ligand moiety would anyway be of different strengths. It was of interest to examine whether thermal method could indicate this difference in bis(acetoacetanilidato)copper(II), [Cu(acacN)<sub>2</sub>], and bis( $\alpha$ -chloroacetoacetanilidato)copper(II), [Cu( $\alpha$ -ClacacN)<sub>2</sub>].

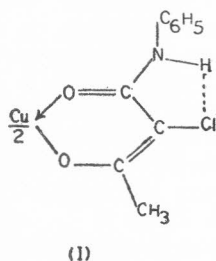
### Materials and Methods

The complexes were prepared as reported elsewhere<sup>8</sup>. Thermograms were obtained (heating rate 4 °C min<sup>-1</sup>) on a Stanton recording thermobalance, model TR-1. For preparing aryl isocyanates, the complexes were heated at 200-250 °C in a micro distillation apparatus, and the condensate collected.

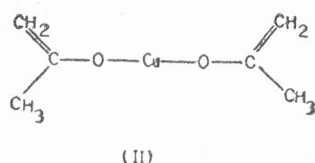
### Results and Discussion

Whereas decomposition of the acetoacetanilide complex commenced at 205 °C, that of the  $\alpha$ -chloroacetoacetanilide complex started only at 225 °C, in air. In the decomposition of [Cu(acacN)<sub>2</sub>], two distinct stages could be observed (Fig. 1). Through independent pyrolytic studies it was shown that in the first stage of decomposition, phenyl isocyanate is removed. The remainder of the complex decomposed between 390 and 500 °C, leaving copper(II) oxide as the residue. In nitrogen atmosphere, decomposition of the complex commenced at slightly higher temperatures (225 and 240 °C respectively), but other characteristics of the thermograms remained practically unchanged. It is thus evident that in static air also it is pyrolysis and not oxidation that occurs.

On the basis of the main contributing structure of acetoacetanilide complex, (I), the features of the thermogram can be explained adequately as follows: The weaker (coordinate covalent) bond (further



weakened by tautomerism attending amide resonance) breaks first followed by breakage of C—C single bond to eliminate phenyl isocyanate<sup>9</sup>. Migration of the NH hydrogen to  $\alpha$ -carbon in this process gives the intermediate product (II).



which then decomposes at a higher temperature. The mass changes at the two stages agreed fully with this explanation. The DTA curve showed two exothermic peaks at 245 and 335 °C. Infrared spectrum of the crude intermediate product in KBr showed a weak band at 3080  $\text{cm}^{-1}$  (olefinic  $\nu\text{C-H}$ ), another weak band at 2910  $\text{cm}^{-1}$  (methyl  $\nu\text{C-H}$ ), a strong and broad band extending from 1620 to 1350  $\text{cm}^{-1}$  ( $\nu\text{C}=\text{C}+\delta\text{C-H}$ ), and two medium intensity bands at 740 and 685  $\text{cm}^{-1}$  (coupled  $\text{Cu-O-C}$  vibration<sup>10</sup>). Thus, the infrared spectrum of the intermediate product is compatible with the proposed structure (II). It appears, therefore, that it is the enolate oxygen that finally ends up as the oxide of copper. X-ray diffraction patterns of the final products obtained in air and in nitrogen atmosphere were identical with that of authentic copper (II) oxide sample. That the two copper-oxygen bonds of acetoacetanilide moiety are of different strengths, thus seems substantiated.

The thermogram of  $[\text{Cu}(\alpha\text{-ClacacN})_2]$  is considerably different from that of  $[\text{Cu}(\text{acacN})_2]$  (Fig. 1). Although, decomposition started at a higher temperature, the ligands were removed in a single accelerated step between 225 and 330 °C. The presence of electron-withdrawing substituent could have hastened the decomposition of the intermediate product, and hence given the semblance of a single step. However, since only one sharp exothermic peak is observed in the DTA curve (at 275 °C), what appears more probable is that the  $\alpha$ -chloro substituent has weakened the otherwise stronger enolate oxygen-metal bond, and strengthened the otherwise weak amide oxygen-copper bond, so that both the metal-oxygen bonds are now somewhat similar in strength, and hence the whole ligand moiety is removed in one step.

**Synthesis through pyrolysis**—As mentioned earlier, controlled pyrolysis of the acetoacetanilide complex yielded phenyl isocyanate, which was identified from its boiling point and conversion to diphenyl urea (m.p.<sup>11</sup> 241 °C). The purity and high yield of the isocyanate obtained prompted us to investigate further the general applicability of preparing aryl isocyanates by this method. Three substituted acetoacetanilide complexes of copper(II) were examined and the method was found to be successful. The operational simplicity which gives the product in high yield and purity (Table 1) adds to the synthetic importance of the procedure. The product in each case was identified from its physical constants<sup>12</sup>.

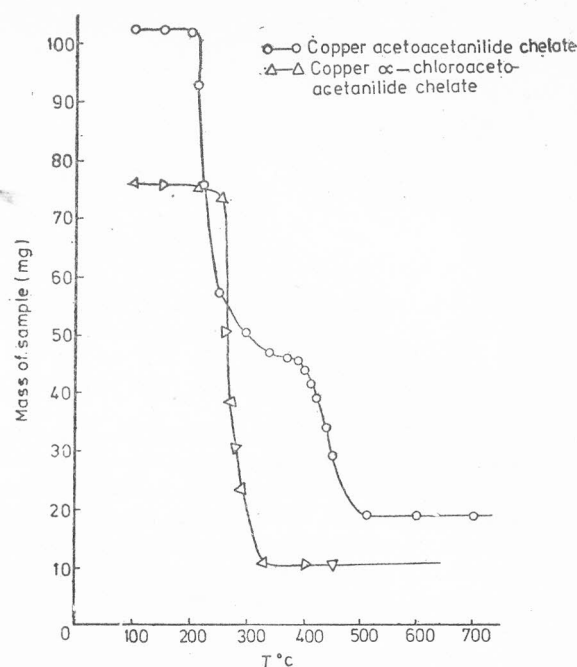


Fig. 1 — Thermograms of copper acetoacetanilide and copper  $\alpha$ -chloroacetoacetanilide chelates.

TABLE 1 — PYROLYSIS OF ACETOACETANILIDE CHELATES OF  $\text{Cu(II)}$

Ligand	Product (yield, %)	b.p. (°C)
Acetoacetanilide	Phenyl isocyanate (83)	165
Acetoacet-2-methyl-anilide	2-Methylphenyl isocyanate (80)	85/27 mm
Acetoacet-4-methylanilide	4-methylphenyl isocyanate (85)	84/24 mm
Acetoacet-4-methoxyanilide	4-methoxyphenyl isocyanate (70)	72-73/20 mm

**Kinetics of thermal decomposition**—The dynamic thermogravimetric data were subjected to analysis by the mechanism invoking Parabolic law, Jander, Ginstling-Brounshtein, Mampel and Avrami equations<sup>3,13</sup>, and the mechanism non-invoking Coats-Redfern<sup>14</sup> equation. In the mechanism based analysis, limited subsequently to Mampel and Avrami equations (since these alone gave reasonable parameters), appropriate functional forms of fractional decomposition,  $g(\alpha)$ , were substituted in the MacCallum-Tanner equation, as demanded by the specific mechanism based equation. Values of  $\log g(\alpha)$  were plotted against  $10^3/T$  (Fig. 2) and the best linear fits were examined further in the light of the kinetic parameters obtained from mechanism non-invoking general kinetic study to arrive at the probable operating mechanism. These results in brief are given in Table 2.

Activation energy for the first stage of decomposition of the acetoacetanilide chelate, is about double that for the single step decomposition of

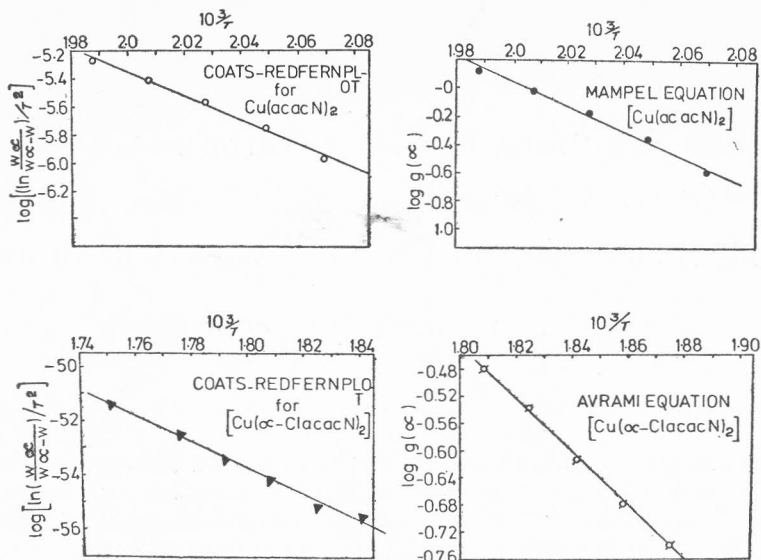


Fig. 2 — Plots of  $1/T$  against  $\log g(\alpha)$  and  $1/T$  against  $\log \left[ \left( \ln \frac{w_0}{w_0-w} \right) / T^2 \right]$

TABLE 2 — KINETIC PARAMETERS OF THERMAL DECOMPOSITION

Compound	Coats-Redfern equation			Mechanistic study		
	$E_a$ (kJ mol <sup>-1</sup> )	$\Delta S^*$ (J deg <sup>-1</sup> mol <sup>-1</sup> )	$Z$	$E_a$ (kJ mol <sup>-1</sup> )	$Z$	Type of equation
[Cu (acacN) <sub>2</sub> ] (Stage 1)	172.3	53.4	$6.3 \times 10^{15}$	164.1	$4.4 \times 10^{14}$	Mampel
[Cu ( $\alpha$ -ClacacN) <sub>2</sub> ]	92.5	-131.8	$1.5 \times 10^6$	92.1	$5.2 \times 10^5$	Avrami

$$g(\alpha) = -\ln(1 - \alpha) \text{ for } [\text{Cu}(\text{acacN})_2], \text{ and } g(\alpha) = 1 - (1 - \alpha)^{1/3} \text{ for } [\text{Cu}(\alpha\text{-ClacacN})_2]$$

$\alpha$ -chloroacetoacetanilide chelate, although decomposition of the latter commences at a higher temperature. This shows that there need not necessarily be any direct correlation between activation energy and thermal stability<sup>15</sup>, particularly when the mechanistic modes also differ. The change of entropy from  $\sim 50 \text{ J deg}^{-1} \text{ mol}^{-1}$  for the acetoacetanilide chelate to  $\sim -130 \text{ J deg}^{-1} \text{ mol}^{-1}$  for  $\alpha$ -chloroacetoacetanilide chelate would mean that the activated complex of the latter has a far more ordered configuration than that of the former.

This investigation points also to the undesirability of inferring probable mechanism from formal similarity of metal chelates.

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