Kinetics of Thermal Decomposition of Copper Soaps

K. N. MEHROTRA, V. P. MEHTA, and T. N. NAGAR
Department of Chemistry, University of Jodhpur, Jodhpur, India
(Z. Naturforsch. 28b, 90—92 [1973]; received August 2/August 22, 1972)

The thermal decomposition of copper soaps has been studied both as a function of temperature and time. The whole range of the isothermal decomposition of copper soaps has been most adequately expressed by the Prou t-T om pkins equation using two different rate constants.

In a previous communication the decomposition of barium soaps was studied both as a function of temperature and time. In the present work a systematic study of the kinetics of the thermal decomposition of copper soaps has been undertaken and attempts have been made to test the validity of well known kinetic equations to account for the complete course of decomposition.

Experimental

Preparation of Soap

Copper soaps were prepared by direct metathesis of the corresponding sodium soap with slight excess of the required amount of copper sulphate solution at 50—55 °C under vigorous stirring. The green precipitate thus obtained was filtered and washed several times with hot distilled water and finally with alcohol to remove the free precipitant and acid, respectively. After initial drying in an air oven at 100—105 °C, the final drying was carried out under reduced pressure. The soaps were further purified by recrystallisation with hot benzene. Copper content of the soap was determined idometrically. The results of elementary analysis were as follows:

Copper caprylate (Found: Cu 18.4; C 54.7; H 8.4, Calcd. for CuC_{16}H_{30}O_{4}: Cu 18.2; C 54.9; H 8.6 %). Copper caprate (Found: Cu 15.9; C 59.0; H 9.2, Calcd. for CuC_{20}H_{38}O_{4}: Cu 15.7; C 59.2; H 9.4 %).

Apparatus

The Stanton thermobalance (Stanton Instrument Ltd., England) is used for the thermogravimetric analysis of copper soaps. It is a deflection type instrument in which dual recorder and a temperature programmer are provided to obtain the change in weight and furnace temperature simultaneously as a function of time on curvilinear chart paper. A change in weight up to 1 g at 1 mg sensitivity or 0.1 g at 0.1 mg sensitivity may be followed and recorded automatically. The simple programmer system gives the rate of heating of about 250 °C per hour.

In all the kinetic studies, the weight of the soap used in each run was 110 mg.

Results and Discussion

The thermal decomposition of copper soaps has been studied both as a function of temperature and time. The thermogravimetric analysis, t. g. a., has shown that the final residue is cupric oxide and the weights of the residues are almost equal to the theoretically calculated weight of cupric oxide from the

Fig. 1. Thermogravimetric analysis of copper soaps.

1 K. N. MEHROTRA and R. P. VARMA, Indian J. Chem. 9, 703 [1971].

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Requests for reprints should be sent to Dr. K. N. MEHROTRA, Dep. of Chemistry, University of Jodhpur, Jodhpur, India.
molecular formulae of the soaps. The plots of the soap residues against the temperature (Fig. 1) indicate that the soaps decompose insignificantly up to 240 °C, slowly between 240 °C to 260 °C, then very rapidly up to 310 °C, afterwards very slowly up to 420 °C and finally show no change with further increase in temperature. It is suggested that the decomposition occurs with the evolution of ketone and carbon dioxide and the overall reaction can be expressed by the equation:

\[
\text{heat} \quad \text{Cu(OOC \cdot R)₂} \overset{\text{heating}}{\rightarrow} \text{RCOR + CuO + CO₂}
\]

\[
\text{Ketone + Cupric + Carbon}
\]

\[
\text{dioxide (Residue)}
\]

It may be pointed out that the final weight of the soap residue decreases with the increase in the chain length of the acid in the soap.

**Isothermal Decomposition of Copper Soaps**

The results of the isothermal decomposition of copper caprylate at 250°, 260° and 300 °C are given in Fig. 2 and are similar to that of copper caprate. It is observed that the fraction of the soap decomposed, \( \alpha \), increases with time, \( t \). The plots of \( \alpha \) against \( t \) show that the fraction of the soap decomposed increases non-linearly with the time in small regions of the initial and final stages of the decomposition and these non-linear regions decrease with the increase in temperature and almost vanishes above 300 °C (Fig. 2).

![Fig. 2. The fraction of copper caprylate decomposed, \( \alpha \), against time, \( t \).](image)

The initial non-linearity is due to the slow reaction stage preceding the acceleratory stage. The intermediate isothermal decomposition at 300 °C is most adequately expressed by an equation:

\[
\alpha = kt + c
\]

where \( \alpha \), \( k \), \( t \), and \( c \) are respectively the fraction of the soap decomposed, rate constant, time, and a constant for the isothermal decomposition of copper soaps.

The middle portions of the plots of \( \alpha \) against \( t \) at 250 °C and 260 °C are characterised by an intersection of two straight lines which may be due to the fact that the rate constants for the acceleratory and decay stages of the isothermal decomposition at these temperatures are quite different. It is, therefore, necessary to use the above equation with two different rate constants, \( k_1 \) and \( k_2 \), to account for the isothermal decomposition of copper soaps at 250 °C and 260 °C.

The values of the rate constants have been calculated from the slopes of the plots of \( \alpha \) against time and are summarised in Table I.

**Tab. I. Values of the rate constants, \( k_1 \) and \( k_2 \), for the isothermal decomposition of copper soaps at different temperatures.**

<table>
<thead>
<tr>
<th>Name of the soap</th>
<th>250 °C</th>
<th>260 °C</th>
<th>300 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( k_1 )</td>
<td>( k_2 )</td>
<td>( k_1 )</td>
</tr>
<tr>
<td>Caprylate</td>
<td>0.04</td>
<td>0.02</td>
<td>0.07</td>
</tr>
<tr>
<td>Caprate</td>
<td>0.04</td>
<td>0.02</td>
<td>0.06</td>
</tr>
</tbody>
</table>

It may be pointed out that the values of the rate constant \( k_1 \) are higher than those of \( k_2 \) which shows that the acceleratory stage is more rapid than the decay stage for the decomposition of these soaps. The rate constants for both the stages increase with the rise in temperature. It is observed that the rate constants, \( k_1 \) and \( k_2 \), for the decomposition of soaps do not vary much with the increase in the chain length of the acid in the soap.

In general the values of the intercepts decrease with the increase in temperature (Table II).

**Tab. II. Values of the intercepts, \( c_1 \) and \( c_2 \), for the isothermal decomposition of copper soaps at different temperatures.**

<table>
<thead>
<tr>
<th>Name of the soap</th>
<th>250 °C</th>
<th>260 °C</th>
<th>300 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( c_1 )</td>
<td>( c_2 )</td>
<td>( c_1 )</td>
</tr>
<tr>
<td>Caprylate</td>
<td>-0.26</td>
<td>+0.08</td>
<td>-0.35</td>
</tr>
<tr>
<td>Caprate</td>
<td>-0.23</td>
<td>+0.04</td>
<td>-0.20</td>
</tr>
</tbody>
</table>

Attempts have been made to test the validity of well known equations derived from the branching and simple interface theories but neither equation holds good and so it is concluded that these theories do not apply to the decomposition of copper soap units entirely.

**Prout-Tompkins, PT, equation** \(^2\) has been
applied to the results of the t.g.a. of the soaps to describe the whole course of the decomposition. The PT equation is written as:

$$\log \left[ \frac{\alpha}{1-\alpha} \right] = Kt + C$$

where $\alpha$ is the fraction of the soap decomposed at time $t$, $K$ is rate constant, and $C$ is a constant. The plots of $\log \left[ \frac{\alpha}{1-\alpha} \right]$ against time (Fig. 3), are characterised by an intersection of two straight lines which shows that the decomposition proceeds in two stages. Therefore, it is necessary to use two equations with two different rate constants $K_1$ and $K_2$ to account for the whole course of the decomposition of copper soaps.

The rate constants for the acceleratory and decay stages for the decomposition of copper soaps at different temperatures have been evaluated from the slopes of the plots of $\log \left[ \frac{\alpha}{1-\alpha} \right]$ against time and are summarised in Table III.

<table>
<thead>
<tr>
<th>Name of the soap</th>
<th>250 °C</th>
<th>260 °C</th>
<th>300 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$K_1$</td>
<td>$K_2$</td>
<td>$K_1$</td>
</tr>
<tr>
<td>Caprylate</td>
<td>0.58</td>
<td>0.10</td>
<td>0.60</td>
</tr>
<tr>
<td>Caprate</td>
<td>0.54</td>
<td>0.09</td>
<td>0.60</td>
</tr>
</tbody>
</table>

The rate constant for the acceleratory stage of the decomposition, $K_1$, is higher than that for the decay stage, $K_2$. The rate constants for both the stages increase with the rise in temperature but do not vary much with the increase in the chain length of the acid in the soap.

The values of the intercepts in the PT equation for the acceleratory and decay stages do not vary much with the temperature. The values of the intercepts for the acceleratory stage of the decomposition of copper soaps are almost constant and independent of the number of carbon atoms in the soaps whereas the values of the intercepts for the decay stage show variation with the increase in the chain length of the soap (Table IV).

<table>
<thead>
<tr>
<th>Name of the soap</th>
<th>250 °C</th>
<th>260 °C</th>
<th>300 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$C_1$</td>
<td>$C_2$</td>
<td>$C_1$</td>
</tr>
<tr>
<td>Caprylate</td>
<td>-6.4</td>
<td>-1.7</td>
<td>-6.3</td>
</tr>
<tr>
<td>Caprate</td>
<td>-6.5</td>
<td>-2.0</td>
<td>-6.3</td>
</tr>
</tbody>
</table>

P r o u t - T o m p k i n s theory, therefore, accounts for the course of the complete decomposition of the soaps but in general two equations with different rate constants are necessary.

P r o u t - T o m p k i n s theory accounts for the whole reaction by assuming that the branching occurs as a result of lateral strains set up in the crystal and these are relieved by the formation of cracks along which decomposition is favoured and further cracking is produced by more strains caused by the decomposition. The reaction thus spreads deeper into the crystal.

It is suggested that the rate controlling factor in the decay stage of the decomposition of soaps is the number of the decomposed molecules and the decomposition is favoured in those molecules which are adjacent to the products.

The authors are thankful to Prof. R. C. K a p o o r, D. Sc., D. Phil., F. N. A. Sc., Head of the Chemistry Department, University of Jodhpur, Jodhpur for his keen interest and valuable criticism throughout the present investigations. One of the authors (T. N. N.) is grateful to CSIR, New Delhi for the research fellowship award.

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The authors are thankful to Prof. R. C. Kapoor, D. Sc., D. Phil., F. N. A. Sc., Head of the Chemistry Department, University of Jodhpur, Jodhpur for his keen interest and valuable criticism throughout the present investigations. One of the authors (T. N. N.) is grateful to CSIR, New Delhi for the research fellowship award.