THE EFFECT OF CATALYSTS ON THE DECOMPOSITION
OF TRISETHYLENE DIAMINE CHROMIUM(III) TRICHLORIDE

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The thermal decomposition of trisethylene diamine chromium(III) trichloride in an
inert atmosphere has been shown to be catalysed by ammonium chloride but not by
ammonium bromide or ammonium iodide as suggested by a previous worker. The
details of sample presentation can effect the results and the presence of oxidising con-
ditions may have influenced previous work.

The role of ammonium chloride as a catalyst is believed to be through its dissociation
into hydrogen chloride and ammonia. The former is an active Lewis acid in the catala-
ytic process.

The activation energies of decomposition are for pure salt $175 \pm 15$ J mol$^{-1}$, in
the presence of ammonium chloride $128 \pm 15$ J mol$^{-1}$ and with hydrogen chloride
gas $79 \pm 15$ J mol$^{-1}$.

The thermal decomposition of the trisethylene diamine salts, Cr(en)$_2$X$_3$nH$_2$O,
where X = Cl, Br, I and SCN, has been the subject of several investigations. Pfeiffer first reported [1] that the chloride and thiocyanate derivatives decomposed
to the cis-bisethylene diamine chromium(III) dichloro chloride and the trans-
bisethylene diamine chromium(III) dithiocyanato thiocyanate respectively. Rollin-
son and Bailar [2] found that these last two reactions were catalysed by ammonium
chloride and ammonium thiocyanate respectively. They also reported that the salts
were sensitive to light, a fact confirmed by Stembridge [3].

Bear and Wendlandt [4] measured the kinetics of the deammination reactions
on single thermogravimetric curves obtained under dynamic conditions and with
air present, the kinetic parameters were obtained by application of the Freeman
and Carroll [5] approach. For uncatalysed Cr(en)$_2$Cl$_3$ and Cr(en)$_2$(SCN)$_3$, the
activation energies and "orders of reaction" were $105$ J mol$^{-1}$, $n = 0.8$ and
$182$ J mol$^{-1}$, $n = 0.7$ respectively. When the trischloride salt was catalysed by
ammonium chloride the activation energy became $88$ J mol$^{-1}$ and the "order"
was 0.5. Interestingly the trithiocyanate salt catalysed by ammoniumthiocyanate
showed a more marked change in activation energy, now $75.5$ J mol$^{-1}$ with the
"order" remaining at $n = 0.7$.

Further to the above, another worker [6] has reported an activation energy of
$192$ J mol$^{-1}$ and "order" $n = 0$ for the trischloride salt decomposed in vacuum
in the absence of catalyst. In the presence of ammonium chloride the activation
energy is $136$ J mol$^{-1}$ and the "order" remains $n = 0$. 
The application of the concept of order of reaction to solid state decompositions has doubtful validity [7, 8], it merely becomes an exponent in a rate equation which provides a fit to the observed data. Also these last authors did not explain the apparent fractional values of n and the mechanism of catalysis was not discussed.

The present work was carried out in order to investigate the apparent discrepancies in the literature regarding the kinetic parameters and to investigate further the mechanism of the catalysis of the chloride salt.

**Experimental**

The trisethylene diamine chromium(III) trichloride was prepared by the standard method [9]. The material was recrystallised twice from alcohol/water and analysis gave Cr 13.00 (13.00), C 18.31 (17.79), H 7.74 (7.93); the figures in ( ), wt %, being the theoretical values for Cr(en)₃Cl₃·3.5H₂O. The anhydrous salt was prepared from the hydrate by stirring with dimethoxy propane for five hours; then drying at 323K for 24 hours; analysis gave: Cr 15.35 (15.40), C 21.45 (21.25), H 7.20 (7.09); where ( ) is theoretical for the anhydrous salt. The crystals of both the hydrate and anhydrous salts were hexagonal rods, average length about 1 mm.

Catalysts were "added" to separate batches of the complex by recrystallising from a 1% solution of the appropriate ammonium salt in the alcohol/water mixture.

The salts were stored in dry atmospheres away from light.

**Apparatus**

Thermal decompositions were carried out using a Stanton thermobalance (HT-M) adapted for gas flows [10]. Samples were presented either in crucibles (Pt/Ir ~ ca. 10 mm high, 10 mm I. D.) or spread on a platinum tray. Dry cylinder Argon (British Oxygen Ltd) could be passed over the sample at 0.150 dm³ min⁻¹ and this gas flow could be dosed with varying concentrations of either dry ammonia or dry hydrogen chloride, from motorized syringes which injected the gases at varying rates into the Argon gas stream. The gases were further mixed in 500 ml flasks containing dry glass wool, and placed in the gas stream prior to the inlet to the apparatus. Only rough estimates, ±2 ppm, were possible for the content of either ammonia or hydrochloric acid in the resultant gas stream.

A technique of operation of the system was adopted so that oxygen and water were eliminated from around the sample; it is estimated that the environment gases contained <2 ppm O₂, <4 ppm H₂O.

For dynamic runs, a heating rate of 1.07 K min⁻¹ was adopted. Sample temperatures were measured to ±0.1 K with the aid of a centre-stem thermocouple.