Journal of Thermal Analysis, Vol. 8 (1975) 99—107

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

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(Received February 8, 1974; in revised form March 25, 1974)

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 conditions 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 catalytic process.

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

The thermal decomposition of the trisethylene diamine salts, $Cr(en)_3X_3nH_2O$, 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. Rollinson 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 $Cr(en)_3Cl_3$ and $Cr(en)_3(SCN)_3$, 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 tristhiocyanate 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 $Cr(en)_3Cl_33.5H_2O$. 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 dm^3 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 O_2, <4 ppm H_2O.

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.

Results

The thermogravimetric curves have been reported in terms of α, the fractional decomposition, versus time. Conversions could be estimated by weight loss to $\pm 1\%$. The sample size was 400.0 mg.

Effect of sample presentation

Fig. 1 demonstrates the bed depth effect found for packed samples, curve *A* for the spread sample gave higher conversion to the bis salt, 96.6% theoretical loss and was significantly different in shape from curve *B* for the packed sample, note the slowing down of the reaction around 80% conversion. Moreover, a lower conversion, at 94%, was found for this last run. Indeed, at the end of the run when reaction had appeared complete, as demonstrated by the arrest on the thermogravimetric curve, the material from the crucible showed an unreacted core of the tris complex.

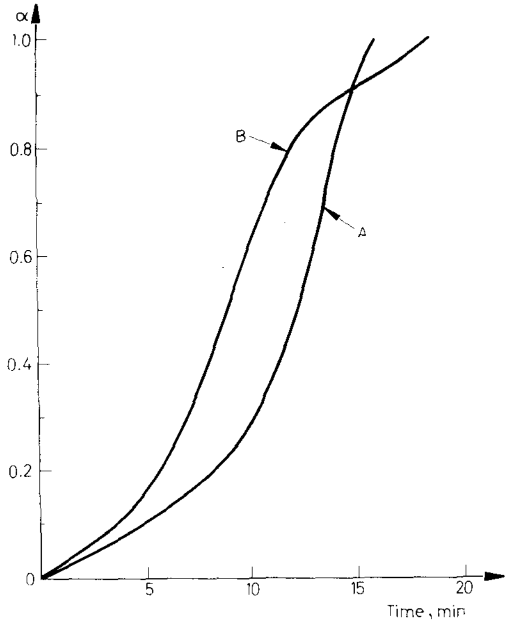

Fig. 1. TG runs on pure $Cr(en)_3Cl_3$. Curve A spread sample, curve B packed sample

Previous workers [4, 6] have presented their samples in crucibles and it is quite possible that bed depth effects could affect the kinetic parameters reported. Therefore, spread samples were used in this work.

Effects of potential catalysts

Results for thermogravimetric runs with various catalysts are given in Fig. 2. For samples with either ammonium bromide or ammonium chloride present the curves were coincidental with the parent curve, *A*, in Fig. 1; they started to lose weight at the same temperature as did the pure tris salt (510 K). It is apparent that, of the catalysts tested, ammonium chloride is the only effective one. It alters the starting temperature of the deamination, now 483 K, and the arrest at 72.5% decomposition is striking; the conversion was now at 101%.

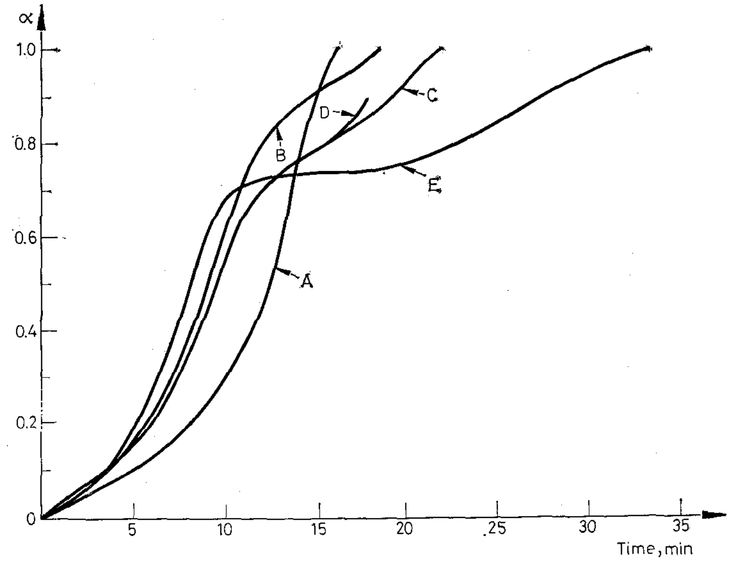

Fig. 2. TG runs on pure $Cr(en)_3Cl_3$ (curve A) and with catalysts present. Curve B pure $Cr(en)_3Cl_3$, packed sample. Curve C, $Cr(en)_3Cl_3$ plus ammonium bromide. Curve D, $Cr(en)_3Cl_3$ plus ethylamine hydrochloride. Curve E, $Cr(en)_3Cl_3$ plus ammonium chloride

The curves have been analysed by the Freeman – Carroll method expressed [7] in terms of α and the plots are given in Fig. 4. The significance and accuracy of the plot is commented on in the discussion. The analysis clearly demonstrates the catalytic activity of ammonium chloride (note: the kinetics of the ammonium chloride experiment are analysed up to 72.5% conversion only).

Because it is possible that ammonium chloride dissociates to ammonia and hydrogen chloride at these temperatures, it was decided to test the catalytic influence of these gases. For argon with ammonia contents of approximately 5, 10, 18 ppm the thermogravimetric curves were coincidental with curve *A*, Fig. 1. However, hydrogen chloride had a marked effect at all concentration levels tested e.g. approximately 3, 7, 15, 22 ppm. Typically for the 7 ppm experiment the curve

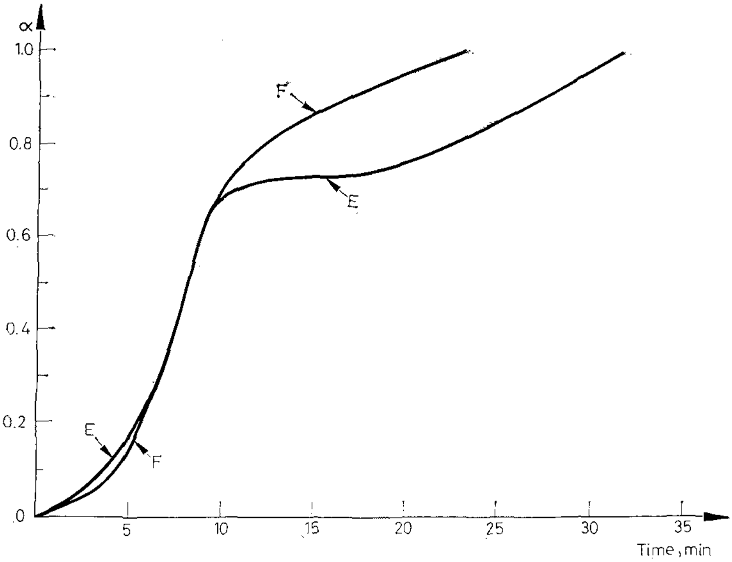

Fig. 3. TG runs on $Cr(en)_3Cl_3$ with catalysts. Curve E, $Cr(en)_3Cl_3$ plus ammonium chloride. Curve F, $Cr(en)_3Cl_3$ plus hydrogen chloride

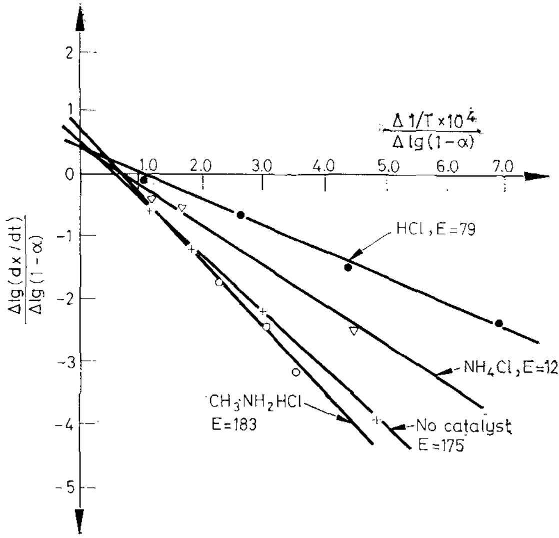

Fig. 4. Analysis of TG curves in Figs 1 and 2 by equation 1

was as F in Fig. 3, here the curve is just about coincidental with the one for the ammonium chloride experiment (E) up to the 72.5% arrest but then conversion is much faster on the last 27.5% of the reaction, the activation energy is strikingly lower at 79 J mol^{-1}. The temperature at the start of the reaction when hydrogen chloride gas is present was further lowered to 479 K.

Discussion

Clarke and Thomas have shown [11] that thermoanalytical techniques under dynamic conditions, may be used to obtain reliable kinetic data. Although other reports [10, 12] suggest that the activation energies from such analyses are significantly higher than those from isothermal experiments. In any event the shape of the thermogravimetric curve, in contrast to those from isothermal experiments where the shape depends only on the reaction mechanism, is seen to be [13] sensitive to heating rate and to the dependence of the rate constant on temperature which in turn involves the parameters of activation energy and frequency factor. Thus the analysis reported here may not be as accurate as that obtained from isothermal experiments but, nevertheless, must give a reasonable indication of the behaviour of the catalysts.

The equation tested on the data and reported in Fig. 4 is of the form [10]

$$\frac{-E^*}{R}\,\Delta\left(\frac{1}{T}\right) = \Delta\ln\left(\frac{-\mathrm{d}\alpha}{\mathrm{d}t}\right) + \left(\frac{1}{n}-1\right)\Delta\ln(1-\alpha)$$

where E^* = activation energy, R = the gas constant, n = the exponent in the Mampel equation [8]; $(1-\alpha) = k(t+K')^n$.

Thus n has real meaning for a model based on a contracting rod, then $n = 2$ and the intercept in the plot of $\dfrac{\Delta\frac{1}{T}}{\Delta\log(1-\alpha)}$ versus $\dfrac{\Delta\log\left(\frac{-\mathrm{d}\alpha}{\mathrm{d}t}\right)}{\Delta\log(1-\alpha)}$ becomes $= 0.5$.

From Fig. 4 it is observed that, within experimental accuracy and with the exception of the system involving methylamine hydrochloride, the intercept approximates to 0.5.

It was possible to interrupt one run on the decomposition of the pure tris salt and to slice crystals so as to expose the reaction interface, a search of the crystals gave one which is represented by the photomicrograph, Fig. 5, and shows an unreacted zone in the centre of the hexagonal rod, thereby confirming a contracting rod model.

The present results are now compared with those of previous workers, Table 1: Bear claimed that all ammonium salts catalysed the reaction, thus from Table 1 the activation energy appears lowered from 105 J.mol^{-1} by about 17 J.mol^{-1}. However, the method he used for winning kinetic parameters would be precise to only ±19 J.mol^{-1}. Also, since the reaction was carried out with oxygen present, the activation energy could be lowered from 192 mol^{-1}, i.e. the result from vacuum experiments, by the products of oxidation; it is known that the salt will oxidise at this temperature. Further, Bear's results arise from samples packed in crucibles.

Table 1

Analysis of kinetic parameters for the thermal decomposition of trisethylene diamine chromium(III) trichloride complex*)

Other workers				This work		
Conditions	'n'	E*	ref. no.	Conditions	'n' ±0.05	E*
pure complex,* salt, crucible	0.8	105	4			
pure complex,* vacuum, crucible	0	192	6	≠ pure complex* argon, spread	0.5	175
complex* + NH_4Cl air, crucible	0.5	88	4			
complex* + NH_4Br air, crucible	0.6	88	4			
complex* + NH_4I air, crucible	0.4	88	4			
complex* + NH_4Cl vacuum, crucible	0	136	6	complex* + NH_4Cl argon, spread	0.5	128
				complex* + HCl gas spread	0.5	79

E^* in J · mol^{-1}, estimated precision ± 15 J · mol^{-1}, also applies to complex* + NH_4Br or + NH_4I, spread and to pure complex* + NH_3 gas, spread.

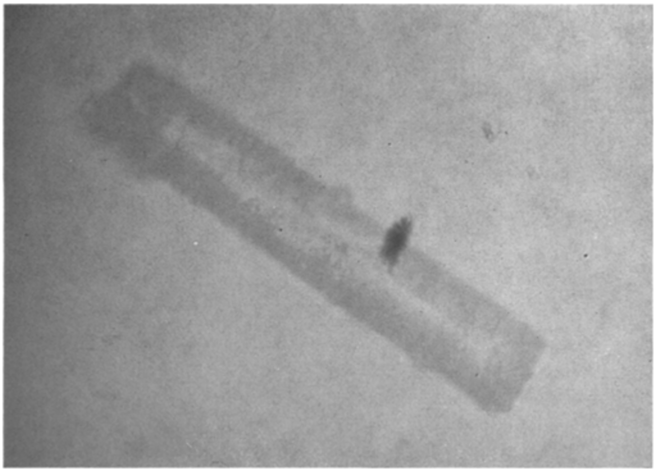

Fig. 5. Photomicrograph of partially reacted tris salt

The activation energy reported here, 175 J.mol^{-1}, is in reasonable agreement with Stembridge's result from vacuum studies, it should be expected that argon atmospheres would be inert with respect to oxidation. However, Stembridge reports an intercept at $n = 0$ which value may be entirely associated with the method of sample presentation e.g. the crystals no longer behave as a collection of hexagonal rods.

The catalytic action of the ammonium chloride could be due to

(i) disordering of the lattice by a phase change in ammonium chloride at the temperature of the reaction; or

(ii) the ammonia and/or hydrochloric acid which will be produced by the dissociation of ammonium chloride at the temperature of the reaction.

Data for various potential catalysts are collected in Table 2.

Table 2

Properties of potential catalysts

	Decomposition temp. [14], K, when $p = 1.32 \times 10^3$ pascals	Sublimation [15] temp. K	M. pt [14] K	Start of* phase change	Start of* dissociation K
NH_4Cl	605	613		457.5	457.5
NH_4Br	661	625		410.8	482
NH_4I	673	824			
CH_3NH_2HCl			500–501		498
en · 2HCl		>543			613

* Found from separate DTA experiments.

If phase change is important, then ammonium bromide and methylamine hydrochloride, as well as ammonium chloride, would be expected to have catalytic activity.

It seems that the dissociation of the catalyst salt is most important. Smith and Calvert [16] give equations for the calculation of the dissociation pressure, at any temperature, for ammonium halides. At 510 K, the start of reaction for the pure complex, the pressures are 34.7 (NH_4Cl), 7.45 (NH_4Br) and 2.57 (NH_4I) pascals $\times 10^{-2}$, whereas at 483 K when reaction starts with NH_4Cl present, the pressures are 14. (NH_4Cl), 2.31 (NH_4Br) and 0.59 (NH_4I) pascals $\times 10^{-2}$. Thus the ammonium chloride undergoes appreciable dissociation at 483 K.

The hydrochloric acid could be operative in two ways. If the reaction were reversible the formation of stable ethylene diamine dihydrochloride would favour decomposition with the bis salt product causing further disruption of the lattice. Separate experiments where the bis salt was added as a catalyst did not enhance the reaction rate. Alternatively, it can be envisaged that the co-ordinated ethylene diamine molecule breaks away from an octahedral site, the vacant site is taken up by a chloride which migrates from a lattice site whilst the free end of the ethylene diamine is stabilised by a proton or hydrogen chloride molecule. There are instances [17] where enH^+ has been identified as a ligand in an octahedral site.

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Résumé — On montre que la dégradation thermique en atmosphère inerte du trichlorure de tris-éthylène-diammine chrom(III) est catalysée par le chlorure d'ammonium mais non par le bromure ou l'iodure d'ammonium, contrairement à ce qui avait été postulé par un autre auteur. Les détails de la présentation de l'échantillon et l'existence de conditions oxydantes peuvent avoir influencer les résultats antérieurs.

On suppose que l'effet de catalyseur du chlorure d'ammonium est dû à sa dissociation en acide chlorhydrique et en ammoniac. Le premier de ces composés est un acide de Lewis actif sur le processus de la catalyse. L'énergie d'activation de la dégradation s'élève à 175 ± 15 J · mol^{-1} pour le sel pur, à 128 ± 15 J · mol^{-1} en présence de chlorure d'ammonium et à 79 ± 15 J · mol^{-1} en présence d'acide chlorhydrique.

Zusammenfassung — Es konnte gezeigt werden, daß die thermische Zersetzung von Tris-äthylendiamin-Chrom(III)-trichlorid in inerter Atmosphäre von Ammoniumchlorid katalysiert wird, nicht jedoch von Ammoniumbromid oder Ammoniumjodid, wie von anderen früher angenommen wurde. Die unterschiedliche Vorbereitung der Probe kann die Ergebnisse beeinflussen und oxidierende Bedingungen sich bei früheren Arbeiten ausgewirkt haben.

Es wird angenommen, daß die katalysierende Rolle des Ammoniumchlorids durch seine Dissoziation in Chlorwasserstoff und Ammoniak hervorgerufen wird. Erstere wirkt als eine aktive Lewis-Säure im katalytischen Prozeß. Die Aktivierungsenergien für das reine Salz 175 ± J · mol^{-1}, in Gegenwart von Ammoniumchlorid 128 ± J · mol^{-1} und in Gegenwart von Chlorwasserstoff-Gas 79 ± 15 J · mol^{-1}.

Резюме — Было показано, что термическое разложение триэтилен-диаминтреххлористого хрома в инертной атмосфере катализируется хлоридом аммония, но не бромидом или иодидом аммония, как было предположено в более ранней работе. Результаты предыдущей работы были обусловлены деталями приготовления вещества и наличием условий для окисления. В настоящей работе предположено, что роль хлорида аммония, как катализатора, обусловлена диссоциацией его на хлористый водород и аммиак. Первый из них выступает в каталитическом процессе в роли активной кислоты Льюиса. Энергии активации разложения чистой соли 175 ± 15 дж · моль^{-1}, в присутствии хлорида аммония 128 ± 15 дж · моль^{-1}, а в присутствии газообразного хлористого водорода 79 ± 15 дж · моль^{-1}.