STUDY OF THE REACTION OF GUANIDINE-NITRATE FROM UREA AND AMMONIUM NITRATE USING SILICA GEL AS CATALYST

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ABSTRACT

The optimum temperature for the maximum yield of guanidine nitrate from urea and ammonium nitrate using Silica gel as catalyst and with a given ratio of urea and ammonium nitrate has been worked out. The kinetics of the reaction leading to the formation of NH_3 have been studied and from the kinetics of the reaction a probable mechanism for the reaction has been suggested.

INTRODUCTION

A METHOD for the preparation of guanidine nitrate from urea and ammonium nitrate using silica gel as a catalyst has been reported by the Pittsburg Coke and Chemical Company, USA. The present work has been carried out with a view to establish the optimum temperature for maximum yield and suitable conditions for the continuous production of guanidine nitrate.

Experiments have been carried out at different temperatures with the ratio of Urea : Ammonium nitrate : Silica gel as 6 gms; 8 gms, 3 gms. (Molar ratio 2 : 2 : 1), the grist size of silica gel being 16/30 mesh (B.S.S.).

The rate of evolution of ammonia and hence the kinetics of the reaction leading to the formation of ammonia have also been studied. The equation for the overall reaction may be given as :

$$2(NH_2)_2CO + NH_4NO_3 = (NH_2)_2\,C:NH\cdot HNO_3 + 2\,NH_3 + CO_2$$

In which one molecule of urea is converted to guanidine by dehydration followed by ammination whilst the other molecule of urea is hydrolysed to give the stoichiometric amounts of ammonia and carbon dioxide.

EXPERIMENTAL

The reaction vessel was a special type of flask which was heated to the required temperatures in a thermostat containing mineral jelly. Weighed amount of silica gel of grist size 16/30 mesh (B.S.S.) and preheated at 140°C for 2 hours was then transferred to the reaction flask. Weighed amounts of urea and ammonium nitrate were mixed and heated to 120°C and then this molten (liquid) mixture was poured into the reaction flask. The amount of ammonia was estimated by passing it through known quantity of sulphuric acid for some definite time interval and then titrating back the excess of acid. The average time for each reaction was 3 hrs. The guanidine nitrate formed was estimated as picrate according to the method of Vozarik,[1] as modified in the C.S. Specification (CS 1299).

In experiments on the kinetics of the formation of ammonia gas it was assumed that ammonia was formed by the decomposition of urea alone and the amount of urea remaining at any stage was calculated from the amount of ammonia on the basis that when two molecules of urea are decomposed two molecules of ammonia are formed.

Qualitative Analysis of the Reaction Mixture

Qualitative analyses of the reaction mixture were carried out at different times during the progress of the reaction at a temperature of 190°C.

The results show that cyanamide, guanyl urea, biuret and cyanate are not present at any stage, whereas the presence of dicyandiamide and biguanide in minute quantities as also guanidine salts were detected at all stages from 1/2 hrs. to 3 hrs. of the reaction time.

RESULTS

The results regarding guanidine nitrate formation are given in Table 1 below:—

TABLE 1

	Percentage of Guanidine Nitrate based on urea					
Temp. °C	150°	160°	170°	180°	190°	200°
Expt. I ..	8·43	21·05	42·6	65·6	78·21	76·1
Expt. II ..	9·94	23·18	38·5	67·83	79·62	

The values of log $a/(a-x)$ have been plotted against time at different temperatures (Fig. 1) where 'a' is the initial concentration of urea in gms. and $(a-x)$ is the concentration after time 't' in minutes. The curves (Fig. 1) so obtained were straight lines which

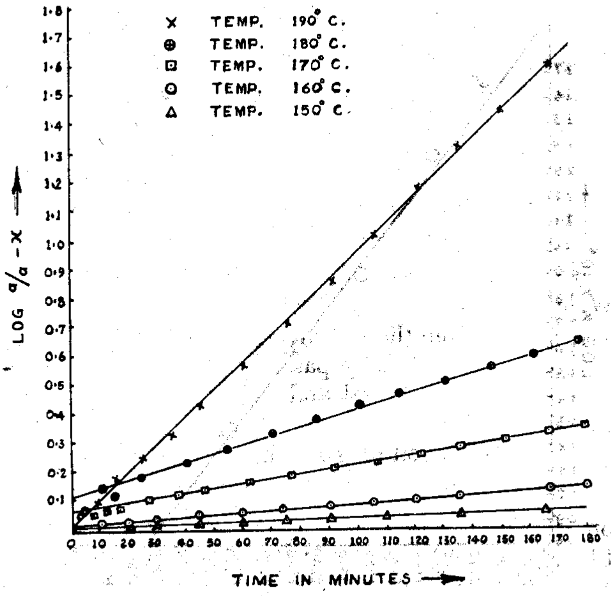


Fig. 1

seems to indicate that the reaction leading to the formation of ammonia apparently obeys the first order law. From the slopes of the curves the values of '*k*', the velocity constant of unimolecular reaction were calculated in each case and the results obtained are given below in Table 2.

TABLE 2

T	I/T	k.	Log.k
423	0·002364	0·0006954	$\bar{4}{\cdot}8422$
433	0·002309	0·001781	$\bar{3}{\cdot}2206$
443	0·002257	0·0039275	$\bar{3}{\cdot}5942$
453	0·002208	0·007616	$\bar{3}{\cdot}8817$
458	0·002183	0·01227	$\bar{2}{\cdot}0888$
463	0·002160	0·02315	$\bar{2}{\cdot}3645$
473	0·002114	0·04746	$\bar{2}{\cdot}6764$

By plotting log *k* against *1/T* (Fig. 2) where *k* is the velocity constant per minute and *T* is the absolute temperature, the Energy of Activation for the reaction leading to the formation of ammonia was calculated and found to be 32,000 calories.

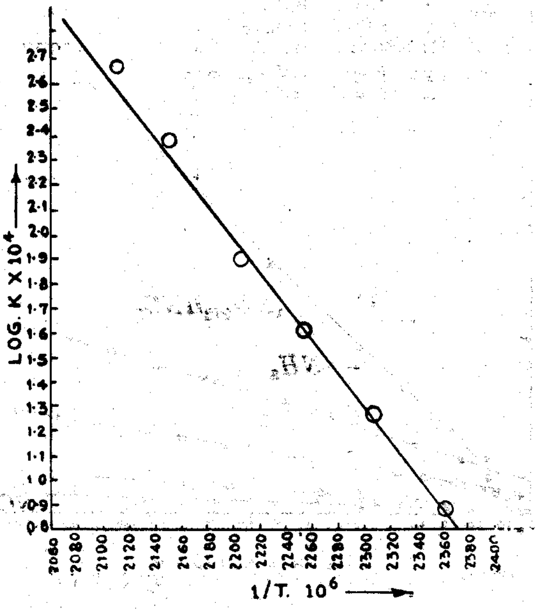


Fig. 2

DISCUSSION

The maximum yield of guanidine nitrate is obtained at 190°C for a total heating period of 3 hrs. At 200°C the yield seems to decrease. The yield of guanidine nitrate decreases when the period of heating at 190°C was raised from 3 to 4 hrs. At higher temperatures the separation of insoluble material was more and this caused some frothing in the reaction vessel.

The continued reuse of silica gel in successive runs was also found to be possible and after three successive uses the silica gel still maintained the effectiveness and the average yield of guanidine nitrate per run was about 80% calculated on the weight of urea taken.

The reaction leading to the formation of ammonia seems to obey the unimolecular law with respect to urea. Burrow and Fawsitt[2], have shown that the apparent hydrolysis of urea by water alone or by aqueous solutions of acids obeys the unimolecular law and the reaction occurs in two stages. The first stage is the slow conversion of urea into ammonium cyanate followed by the rapid hydrolysis of ammonium cyanate into ammonia and carbon dioxide.

$$CO\,(NH_2)_2 \rightleftharpoons NH_4\,OCN$$

$$NH_4OCN + H_2O \longrightarrow 2\,NH_3 + CO_2$$

The authors believe that a small amount of decomposition of carbamide may go on but is not appreciable. From Burrow and Fawsitt's velocity constants for the decomposition of urea at 61·1°, 71·3° and 98·2°C the critical increment has been calculated by Moelwyn-Hughes[3] and found to be 31,300 calories. The critical increment as found by us for the ammonia formation in urea ammonium nitrate reaction has been found to be 32,000 cals. This seems to indicate that the formation of ammonia in the reaction between urea and ammonium nitrate in presence of silica gel catalyst is due to the hydrolysis of urea by the water formed in the dehydration of urea.

The reaction seems to proceed according to the following mechanism:—

$$CO\,(NH_2)_2 \longrightarrow CN\cdot NH_2\ \mathrm{H_2O} \qquad (1)$$

$$CN\cdot NH_2 + NH_4NO_3 \longrightarrow HN = C(NH_2)_2HNO_3 \qquad (2)$$

$$CO\,(NH_2)_2 + H_2O \longrightarrow CO_2 + 2NH_3 \qquad (3)$$

The overall reaction is :

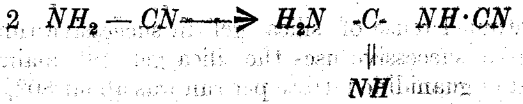
$$2\,CO\,(NH_2)_2 + NH_4\,NO_3 \longrightarrow HN = C\,(NH_2)_2\,HNO_3 + 2\,NH_3 + CO_2$$

The dehydration of urea by silica gel to form cyanamide and dicyandiamide is the subject of a recent patent by the American Cynamide Co[4]. and has also been verified in this laboratory.

Since cyanamide could not be detected in the reaction mixture, the step (2) may be a very fast one at the temperature concerned. The formation of insoluble products such as melamine, ammelide etc. < and biguanide may take place by side reactions as follows :—

$$3\ H_2N - CN \longrightarrow C_3N_6H_6$$

(Melamine)



$$2\ NH_2 - CN \longrightarrow H_2N-\underset{\underset{NH}{\|}}{C}-NH\cdot CN$$

(Biguanide)

$$(NH_2)_2CO \rightleftharpoons NH_4OCN \rightleftharpoons HOCN + NH_3$$

$$2\,H_2N\cdot CN + HOCN = C_3H_5ON_5$$

(ammelide)

Although, no cyanamide could be detected in the melt, the presence of biguanide and dicyandiamide have been confirmed. Moreover, it was observed that the ratio of NH_3/GN was higher at 150°C (Ca 3·4) and lower at 190°C (Ca 2·5). This indicates that the production of ammonia is always higher than the stoichiometric value and approaches towards the ideal value of 2 at higher temperatures, although with increase of temperature, the extent of direct decomposition of urea into ammonia and carbon dioxide may possibly increase.

Acknowledgement:—The authors thank the Research and Development Organisation, Ministry of Defence, for granting permission for the publication of this work.

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