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SOME REACTIONS OF THE AZOTETRAZOLE ANION WITH DILUTE MINERAL ACIDS

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EXPLOSIVES RESEARCH AND DEVELOPMENT ESTABLISHMENT

TECHNICAL NOTE No. 44

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SUMMARY

The reactions of the azotetrazole (5,5'-azoditetrazole) anion with dilute nitric, sulphuric, hydrochloric, phosphoric, perchloric, acetic, carbonic acids and acidic ceric ammonium nitrate have been investigated.

The degradation of the azotetrazole anion by dilute hydrochloric and dilute sulphuric acids has been confirmed to give 5-hydrazinotetrazole as proposed by Thiele. However other high nitrogen products have also been isolated; one of which is explosive. With dilute nitric acid the degradation gave, as well as gaseous products, 5-azidotetrazole whose salts, especially that of silver, are hypersensitive to mechanical stimulus. An Appendix giving details of the infrared spectra of 5-azidotetrazole and related compounds is included.

CONTENTS

Reference: WAC/214/014

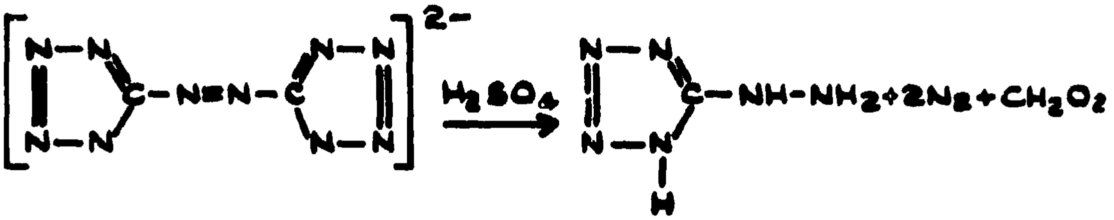
1 INTRODUCTION

1 1 Object

There is an established need for a stab-sensitive composition which cannot segregate and has high thermal and chemical stability. A single-component composition developed in ERDE, monobasic lead azotetrazole, RD 1355, very nearly satisfies current UK requirements for such a composition but in the present devices it is not quite sensitive enough. The work described below arose out of endeavours to increase the stab-sensitivity of RD 1355 by co-crystallization of it with the much more sensitive silver azotetrazole salt. In the course of this investigation a hypersensitive silver composition was generated which gave rise to an incident when being filled into Rotter caps for sensitiveness tests. This incident is fully described in the report of the enquiry.[1] In the course of this enquiry it became obvious that one of the recommended methods for destruction of azotetrazole salts, by treating with dilute nitric acid,[2] gives rise to solutions which contain an explosive component and which forms, when reacted with silver nitrate, the hypersensitive silver salt mentioned above. The object of this Note is to describe the work carried out to establish the nature of the reaction products from the reaction of the azotetrazole (5,5'-azoditetrazole) anion with dilute acids, especially dilute nitric acid.

1 2 Previous Studies

Although the metallic salts of the azotetrazole anion have received consideration from the technical aspect as initiatory compositions[2,3] there is very little reported chemistry of this anion other than that of the original work of Thiele in which he describes the reactions with boiling dilute sulphuric acid, oxalic acid, bromine and its reduction to 5,5'-hydrazotetrazole.[4] The reaction of interest is that with boiling dilute sulphuric acid which he claims to give 5-hydrazinotetrazole, nitrogen and formic acid as below:



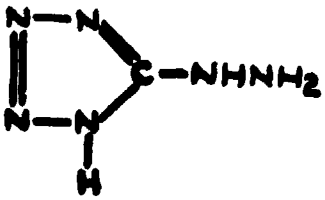
5-hydrazinotetrazole does not decompose readily in acid solution but will decompose at 170°C in hydrochloric acid to carbon dioxide, nitrogen and hydrazine.[5]

This investigation considered the reactions of the azotetrazole anion with primarily, dilute hydrochloric acid, sulphuric acid and nitric acid.

2 EXPERIMENTAL

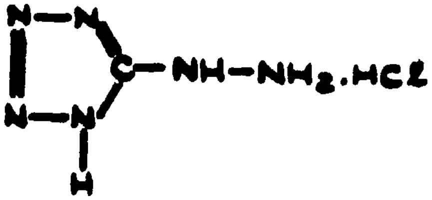
2 1 Preparation of Reference Compounds

2 1 1 5-Hydrazinotetrazole



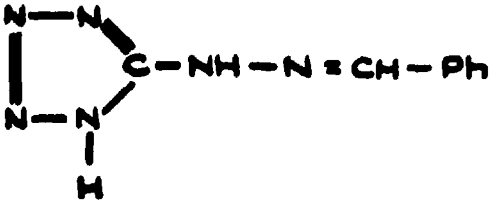
To a solution of disodium azotetrazole pentahydrate (10.0 g) suspended in water (100 ml) was added hydrochloric acid (25 ml 5N). The solution was warmed on a water bath until the gas evolution finished, then was evaporated to dryness from water three times to remove the hydrochloric acid. The residue was dissolved in a minimum of hot water and a hot solution of sodium acetate (10.0 g) in water (10 ml) was added. The apparatus was flushed out with carbon dioxide and the solution allowed to cool to give 5-hydrazinotetrazole as white prisms with a yield of 2.5 g, mp 195 - 8°C (lit 199d).

2 1 2 5-Hydrazinotetrazole Monohydrochloride



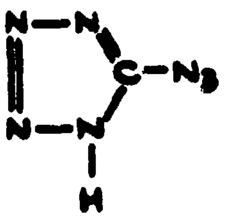
Hydrochloric acid gas was passed slowly through a solution of 5-hydrazinotetrazole (1.0 g) in water (5.0 ml) for 10 minutes. The water was removed by evaporating the solution in a desiccator over concentrated sulphuric acid to give the monohydrochloride as colourless needles.

2 1 3 The Benzal of 5-Hydrazinotetrazole



To a suspension of disodium azotetrazole pentahydrate (6.0 g) in water (25 ml) was added hydrochloric acid (30 ml 5N). When the reaction had apparently ceased the solution was warmed on a water bath and a solution of benzaldehyde (2.5 g) in ethanol (10 ml) was added to give a white crystalline precipitate which when recrystallised from a 1:1 ethanol/water mixture had an mp of 235°C (lit 235°C).

2 1 4 5-Azidotetrazole



This compound was prepared by the method of Lieber[6] in which 5-hydrazinotetrazole is reacted with nitrous acid.

2 1 5 Silver 5-Azidotetrazole

Equimolar aqueous solutions of 5-azidotetrazole and silver nitrate were mixed to give a white gelatinous precipitate which was not isolated dry. Its infrared spectra was determined by replacing the water by ethanol to give a slurry which was added to partially milled potassium bromide. The ethanol was then evaporated off at 60°C to give a dry mixture which could be ball milled. The silver salt is extremely sensitive.

2 2 Analysis of Reference Compounds

Compound	%C Calc	%C Found	%N Calc	%N Found	%H Calc	%H Found
5-Hydrazinotetrazole	12.0	11.8	84.0	84.3	4.0	4.0
5-Hydrazinotetrazole monohydrochloride	8.8	9.4	61.6	60.8	3.7	3.7
Benzal of 5-hydrazinotetrazole	51.1	50.6	44.7	44.7	4.3	4.3
5-Azidotetrazole	10.8	11.1	88.3	87.4	0.97	0.91

2 3 Infrared Spectra of Reference Compounds

The spectra recorded in the literature of these compounds are of low resolution and were recorded in Nujol mulls, two peaks of which badly obscure parts of the spectra. This caused considerable delay in the elucidation of the reaction of the azotetrazole anion with dilute nitric acid. In view of this the spectra of these compounds are presented in an Appendix. The characteristic azide absorption appeared at 2150 cm^{-1} for the 5-azidotetrazole and at 2160 cm^{-1} for the silver salt.

2 4 Reactions of Disodium Azotetrazole Pentahydrate ($Na_2AT.5H_2O$) with Acids other than Nitric

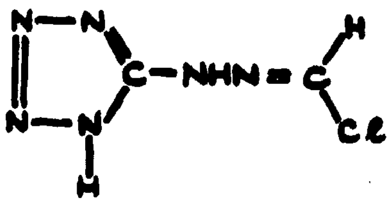
2 4 1 Hydrochloric Acid

It was shown that dilute (5N) hydrochloric acid with $Na_2AT.5H_2O$ gave

5-hydrazinotetrazole by isolation of the tetrazole and by forming its benzal (see Section 2 1 1). This route was found to be convenient for the preparation of 5-hydrazinotetrazole. If the reaction solution was evaporated to dryness then the residue was sodium chloride (shown by X-ray powder pattern) and 5-hydrazinotetrazole hydrochloride.

An intermediate reaction product could be isolated in good yield by the following procedure. $Na_2AT.5H_2O$ (10 g) suspended in water (20 ml) is treated with hydrochloric acid (25 ml 5N) and stirred for 1 hour. White fluffy needles (5 g) are obtained which can be filtered out. After drying over P_2O_5 in vacuo the following analytical results were obtained: C, 16.3; H, 2.07; N, 56.7%. Required for $C_2H_3N_6Cl$: C, 16.4; H, 2.06; N, 57.4%. Treatment of the dry solid with concentrated sulphuric acid gave rise to hydrochloric acid gas. A solution of the solid in water was titrated potentiometrically against 0.10N sodium hydroxide solution. The resulting curve indicated that the solution behaved as a dibasic acid. Formic acid was shown to be present in the aqueous solution of the solid by the chromotropic acid test.[7]

These results can be explained if the solid has the following structure:



On treatment with water this decomposes to give 5-hydrazinotetrazole, formic acid and hydrochloric acid.

2 4 2 Sulphuric Acid

With warm 5N sulphuric acid the product was shown to be 5-hydrazinotetrazole thus confirming Thiele's work. A solid residue could not be obtained but 5-hydrazinotetrazole was isolated practically quantitatively as the benzal. With cold dilute acid, a brown solid was obtained from the reaction and proved to be a sensitive explosive. The brown solid gave the following analytical results: C, 18.4; N, 68.3; H, 2.45% which corresponds to C:N:H ratios of 2:6:3. Its infrared spectrum also suggests the presence of water.

2 4 3 Acetic Acid

Acetic acid was heated with both $Na_2AT.5H_2O$ and monobasic lead azotetrazole, $PbAT.Pb(OH)_2$ (RD 1335). There was very little reaction and even after several days a considerable amount of unreacted material was left.

2 4 4 Ceric Ammonium Nitrate

$Na_2AT.5H_2O$ and $PbAT.Pb(OH)_2$ were heated with 15% w/v ceric ammonium nitrate solution to give a considerable amount of gas and on evaporation a dark residue which was not identified but was shown to be non-explosive.

2 4 5 Carbon Dioxide

Carbon dioxide gas was bubbled slowly through a solution of $Na_2AT.5H_2O$ (1.0 g) in water (100 ml) for 3 weeks, by which time the solution became practically colourless. The solution was divided into 2 parts; with 1 part an attempt to form a benzal was made which was unsuccessful, the remainder was evaporated to give a non-explosive residue.

2 4 6 Phosphoric Acid

Treatment of $PbAT.Pb(OH)_2$ with hot 20% w/v phosphoric acid gave lead phosphate and a colourless liquor. This liquor when treated with silver carbonate gave a non-explosive precipitate which gave no peak at 2160 cm^{-1} in its infrared spectrum thus indicating that there was no silver azidotetrazole present.

2 4 7 Perchloric Acid

Treatment of $PbAT.Pb(OH)_2$ with 5N perchloric acid gave a colourless solution which when treated with silver perchlorate gave an explosive precipitate. Infrared spectral analysis showed that this precipitate contained the perchloric acid radical. Treatment of the liquor with silver carbonate gave a non-explosive precipitate whose infrared spectrum showed no absorption at 2160 cm^{-1}, ie silver azidotetrazole was not present.

2 5 Reaction of $Na_2AT.5H_2O$ with Nitric Acid and Related Nitric Acid Reactions

2 5 1 Isolation of 5-Azidotetrazole from $Na_2AT.5H_2O$ Reaction with Nitric Acid

To a suspension of $Na_2AT.5H_2O$ (2.0 g) in water (10.0 ml) was added nitric acid (40 ml 5N). After the gas evolution had finished the solution was evaporated to dryness to give a residue which was extracted with chloroform. The extract was evaporated to dryness to give an oil which crystallised when toluene was added to it. After recrystallisation from toluene 0.077 g 5-azidotetrazole, as identified by X-ray powder and infrared spectral methods, was obtained as long white needles. A small amount was converted to a silver salt (see Section 2 1 5) which was shown to be identical with that obtained from both 5-azidotetrazole and from the incident with the Rotter caps.[1]

2 5 2 Action of Nitric Acid on Silver Azotetrazole

Silver azotetrazole samples, prepared by the method of Taylor et al,[2] were allowed to stand under 50% and 25% nitric acid solutions for 4 days. The X-ray powder pattern of the resulting product showed that no reaction had occurred.

2 5 3 An Explosion with Silver Nitrate Solution and Hot Solution of $Na_2AT.5H_2O$ and Nitric Acid

A mixture of $Na_2AT.5H_2O$ (4.0 g) in water (20 ml) and nitric acid (80.0 ml 5N) was allowed to react. After standing for 1 hour at ambient temperature a solution of silver nitrate (5.0 g) in nitric acid (20 ml 5N) and water (80 ml) was added slowly to the solution which was now at 55°C A heavy crystalline precipitate formed as the addition proceeded. After about 5 min a click was heard from the reaction solution. The addition was stopped and about a minute later there was a loud explosion.

2 6 Reactions of 5-Hydrazinotetrazole in Nitric Acid Solution

2 6 1 An Explosion from the Reaction of Dilute Nitric Acid and 5-Hydrazinotetrazole

A solution of 5-hydrazinotetrazole (1.0 g) in water (10.0 ml) and nitric acid (20 ml 5N) was evaporated to near dryness on a water bath. As the solution became warm, gas was evolved. The sticky residue was cooled and put into a vacuum desiccator over P_2O_5. After approximately 2 hours there was a loud explosion.

2 6 2 Silver 5-Azidotetrazole from Silver Nitrate, Nitric Acid and 5-Hydrazinotetrazole

A solution of 5-hydrazinotetrazole (0.10 g) in nitric acid (10 ml 5N) was heated on a water bath to almost dryness. Gas was evolved during the evaporation. To the cooled residual solution was added water (10.0 ml) followed by a solution of silver nitrate (0.170 g) in water (2.0 ml) to give a white precipitate. After washing with water, filtering and washing with ethanol a sample was taken for infrared analysis. This showed that the sample was silver 5-azidotetrazole.

2 6 3 Silver Salt of 5-Hydrazinotetrazole

A solution of silver nitrate (0.170 g) in water (3.0 ml) and 5-hydrazinotetrazole (0.099 g) in nitric acid (5 ml 5N) were mixed at ambient temperature to give a white precipitate. Infrared spectra of the precipitate showed that it was not an azide compound and that it contained NO_3^- groups. The analysis gave: C, 4.64; H, 1.22; N, 33.00%.

2 7 Analysis of Gaseous Products

Samples of $Na_2AT.5H_2O$ were decomposed in a vacuum system by various dilute acids. The volume of gas evolved was measured and its constituents analysed by gas chromatographic methods. Dilute hydrochloric acid on $Na_2AT.5H_2O$ gave after 30 min 1.8 moles of N_2 per mole $Na_2AT.5H_2O$. The action of nitric acid (5N) is more complex. After 30 min the following results were obtained.

Gas	Vol % of total		Moles/Mole AT	
	Run (1)	Run (2)	Run (1)	Run (2)
CO_2	11.3	9.9	0.42	0.45
CO	1.9	1.7	0.06	0.08
N_2	85.0	85.0	3.25	3.96
N_2O	2.3	3.5	0.68	0.16

A solution after treatment with nitric acid was evaporated to dryness to remove any formic acid. The residue was dissolved in water and treated with 15% w/v ceric ammonium nitrate in nitric acid 5N. The gaseous products gave the following analysis: N_2, 78.2; CO_2, 5.2; CO, 16.6% 5-azidotetrazole gave: N_2, 77.8; CO_2(CO), 22.2%

3 RESULTS

3 1 A Summary of the reactions carried out and the results is presented in Fig 1 through 3.

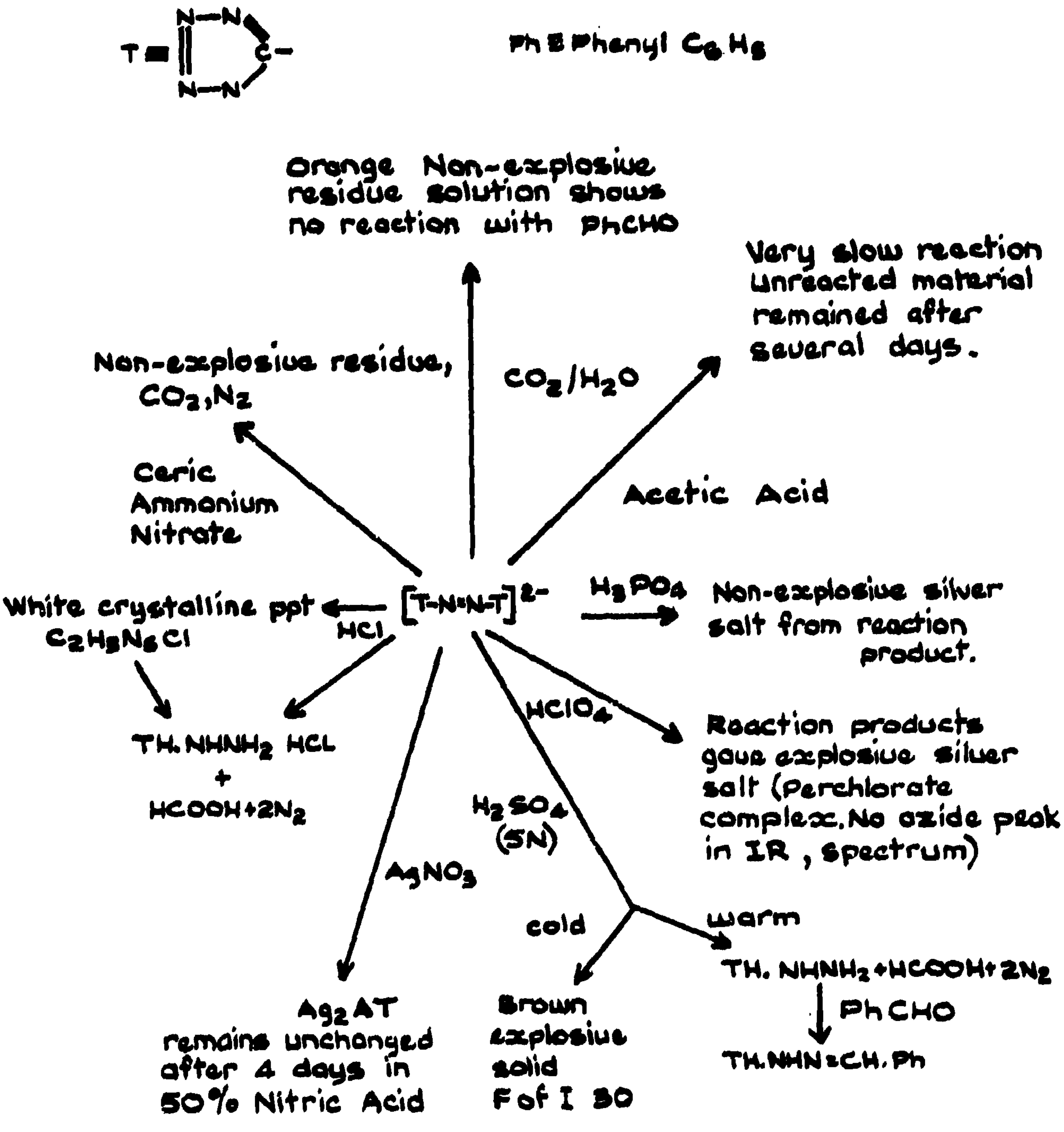


FIG. 1 DEGRADATION OF THE AZOTETRAZOLE ANION With acids other than nitric acid.

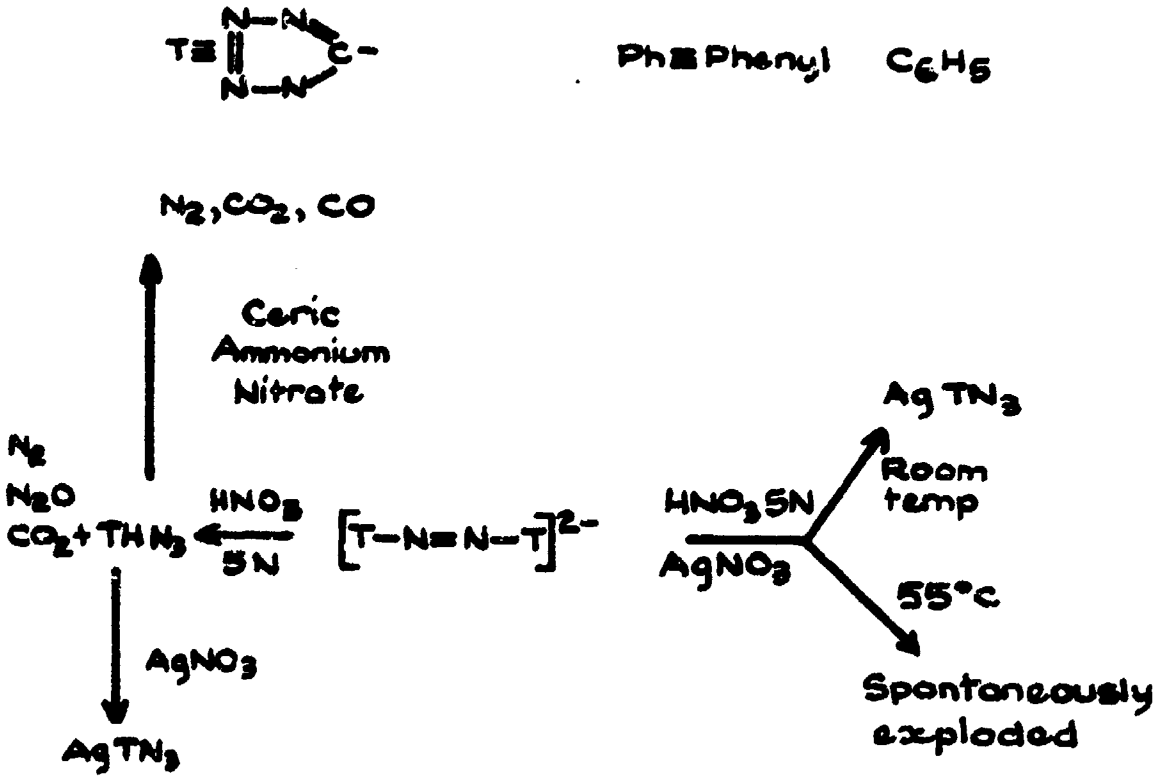


FIG. 2 DEGRADATION OF AZOTETRAZOLE ANION

Reactions with nitric acid

T ≡ 

Ph ≡ Phenyl C_6H_5

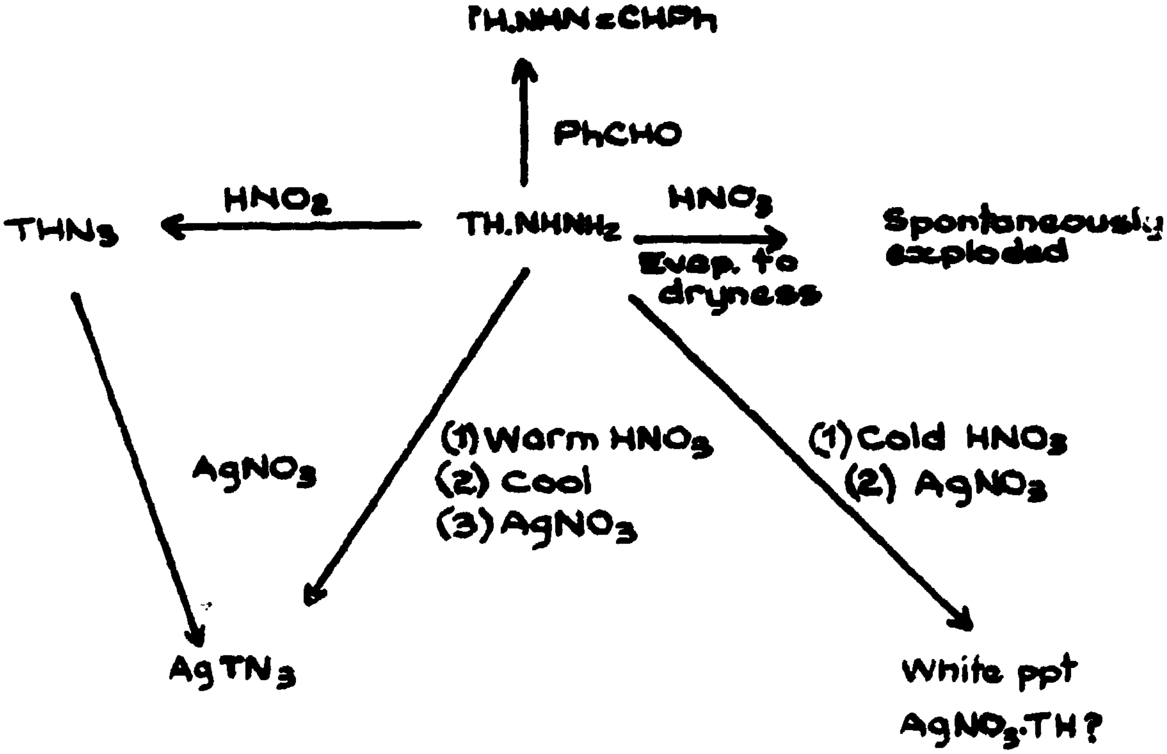


FIG. 3 DEGRADATION OF THE AZOTETRAZOLE ANION

Reactions of 5-hydrazinotetrazole

3 2 Hazards of Residues

The residues from many of the experiments were subject to the following tests: Rotter test, Train test and Friction. The results are given in Table 1.

TABLE 1

SENSITIVENESS OF PRODUCTS AND EVAPORATION RESIDUES

Sample	Rotter Test RMH, cm	Train Test or Hotplate Test	Friction		
			Mild Steel	Naval Brass	Al Bronze
Silver 5-azidotetrazole	Too sensitive to handle. When dry will explode if touched with rubber spatula				
5-Azidotetrazole	Can be handled when dry but very destructive when explodes				
5-Hydrazinotetrazole monohydrochloride	111	Flashes and crackles on hotplate			
Brown product from $Na_2AT + H_2SO_4$ (5N) cold	33	Flash	0/10	2/10 burns	1/10 burns
*$Na_2AT.5H_2O + HNO_3$	192	Exploded on hotplate			
*$Na_2AT.5H_2O + HCl$	88	Crackles, smokes, does not support train	0/10	0/10	0/10
$Na_2AT.5H_2O$ + warm H_2SO_4 (5N)		Hygroscopic Not tested			
*$Na_2AT.5H_2O$ + Ce Amm NO_3	Out of range	No ignition	0/10	0/10	0/10
*$PbAT.Pb(OH)_2$ (RD 1355) + acetic acid	Explodes, unreacted $PbAT.Pb(OH)_2$ present				
*$Na_2AT.5H_2O$ soln + CO_2	Out of range	No ignition			
*$PbAT.Pb(OH)_2$ (RD 1355) + HNO_3 (5N)	111	Exploded on hot plate	0/10	0/10	0/10
*$PbAT.Pb(OH)_2$ (RD 1355) + HCl (5N)	151	Crackles and smokes	0/10	0/10	0/10
*$PbAT.Pb(OH)_2$ (RD 1355) + H_2SO_4 (5N) (recommended method of destruction)		No ignition			

*Evaporation residue

4 DISCUSSION

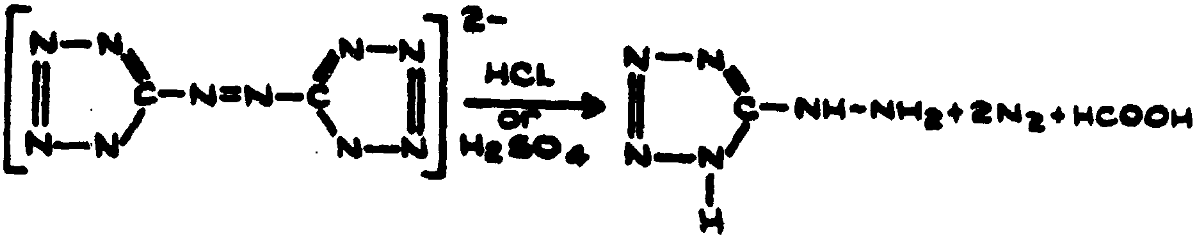
4 1 Reactions of the Azotetrazole Anion with Acids other than Nitric

In the course of this investigation the reactions of the AT anion with dilute sulphuric, hydrochloric, phosphoric, perchloric, acetic, carbonic acids and acidic ceric ammonium nitrate have been looked at mainly from the safety aspect and not from a mechanistic viewpoint. Thus if complex mixtures were obtained the main aim was to determine their hazard rather than consider their constitution in detail. The reaction of both $Na_2AT.5H_2O$ and $PbAT.Pb(OH)_2$ (RD 1355) with acidic (nitric) ceric ammonium nitrate gave gaseous products and a dark, ill-defined residue which was not analysed but was shown to be non-explosive and non-inflammable. Similarly the slow reaction of carbon dioxide in water with the sodium salt gave on evaporation to dryness, a red-brown residue which again was non-explosive. The solution from this reaction did not contain 5-hydrazinotetrazole, as benzaldehyde gave no reaction with it. This reaction of carbon dioxide is of interest because it has been shown that the colour fading effect of dilute solutions of sodium azotetrazole pentahydrate when exposed to the gas is not stopped by buffering the solution with sodium borate. It appears that destruction by carbonic acid is due, at least in part, to some effect other than the induced pH of solution.

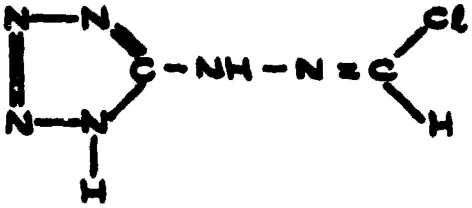
Treatment of the basic lead salt, $PbAT.Pb(OH)_2$ (RD 1355), with phosphoric acid gave a product which did not contain an explosive radical as shown by the examination of material precipitated as the silver salt. However, reaction with 5N perchloric acid gave a colourless solution which on reaction with silver perchlorate gave an explosive precipitate which was most probably a double salt of silver perchlorate as its infrared spectrum showed the presence of the perchlorate anion. If the clear solution from the reaction with perchloric acid was treated with silver carbonate then a non-explosive precipitate was obtained. The reaction with acetic acid proceeded only slowly and complete reaction had not been effected after a week at 90°C.

The earlier work of Thiele was confirmed when it was shown that with warm dilute sulphuric acid the azotetrazole anion gave 5-hydrazinotetrazole, as isolated from solution by the benzal, in practically quantitative yield. The acid salt could not be isolated, the reaction yielding only a sticky ill-defined solid. A product which was not mentioned in Thiele's paper was the brown explosive product that was formed under conditions which have not been fully defined but appeared to be associated with cold reaction solutions. This product must be avoided when using the sulphuric acid destruction method for the azotetrazole anion as it is quite sensitive (RMH 30). Its structure could not be determined although its elemental analysis showed that it had a C:H:N ratio of 2:3:6 and that it contained another element which was probably oxygen from an associated water molecule. Its infrared spectrum suggested the presence of the tetrazole ring and it appeared probable that the substance was either polymeric or a mixture of products.

The reaction of dilute hydrochloric acid with the anion was studied in a little more detail. 5-Hydrazinotetrazole was isolated from the reaction solution as the benzal and in this case a solid monohydrochloride was also isolated. Attempts to make the dihydrochloride as described by Thiele were unsuccessful as they gave the monohydrochloride.[8] The monohydrochloride was identified by its infrared spectrum in the evaporated residues from the reactions of the salts of $Na_2AT.5H_2O$ and $PbAT.Pb(OH)_2$. An analysis of the gases evolved from the reaction of dilute hydrochloric acid with the sodium salt showed that two moles of nitrogen were evolved per mole of azotetrazole anion and that no carbon dioxide was evolved. Thiele showed that the carbon atom from the broken tetrazole ring appears as formic acid.[4] The degradation of the azotetrazole anion by both warm dilute sulphuric acid and dilute hydrochloric can be represented by the following reaction in confirmation of Thiele's proposals.[4]



It is interesting that an intermediate product from the hydrochloric acid reaction has been isolated. This white, crystalline, hygroscopic material most probably has the following structure:



4 2 The Reactions of the Azotetrazole Anion with Dilute Nitric Acid

It must be stated that during the course of this work not only have some very sensitive compounds been obtained but also several spontaneous explosions have occurred and thus it has been necessary to take the maximum precautions throughout. When most metallic salts of the azotetrazole anion are reacted with dilute nitric acid there is a vigorous evolution of gas and in the past this has been taken as a sign of complete destruction such that there is no explosive radical left in solution.[1,2] However the silver salt and possibly the copper salt do not undergo this vigorous reaction. X-ray powder patterns of residues have shown that silver azotetrazole will withstand 50 and 20% nitric acid solutions for periods of at least 4 days and remain completely unchanged. This behaviour may be explained by formation of an inert complex between the silver cation and the azotetrazole anion. The copper salt is also difficult to destroy with nitric acid and a similar explanation is possible. The work described in this Note has demonstrated that the solutions resulting from the destruction of the sodium and monobasic lead salts contain explosive end products as shown by an examination of the evaporated residues (see Table 1) and that a hypersensitive silver salt may be formed when these solutions are treated with silver nitrate.

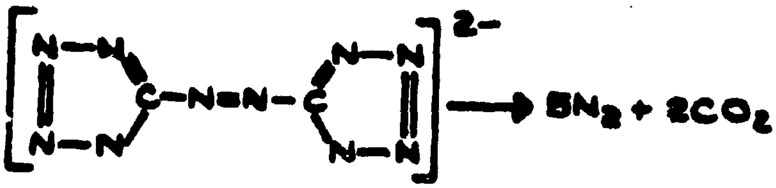
4 2 1 Examination of the Residue after Evaporation

When a solution of disodium azotetrazole pentahydrate ($Na_2AT.5H_2O$) was treated with dilute nitric acid and the solution evaporated to dryness, the infrared spectrum of the residue in a KBr disc showed the presence of sodium nitrate and a constituent with a strong peak at 2150 cm^{-1}; a feature which suggested the presence of an azido group. This constituent was extracted from the inorganic salts with chloroform to give an oil which when treated with toluene crystallized to a white acicular product. This product, which was obtained in 10 to 15% yield, based on the azotetrazole anion, was shown to be 5-azidotetrazole by comparison of its infrared spectrum with that of an authentic sample prepared by the action of nitrous acid on 5-hydrazinotetrazole.[8] Its elemental analysis also corresponded to that required for 5-azidotetrazole. The silver salts of the material obtained from the disodium azotetrazole pentahydrate destruction and 5-azidotetrazole were prepared and shown to be identical by both infrared spectroscopy and by their X-ray powder pattern photographs. The silver salt of 5-azidotetrazole could not be handled when dry as it was so sensitive. A spontaneous explosion occurred during one preparation of silver 5-azidotetrazole. These very hazardous properties of the salts of 5-azidotetrazole have been noted by previous workers.[8] The X-ray powder patterns of the silver salt correspond to that obtained from the residue which was involved in the incident in the Rotter machine room at ERDE.[1]

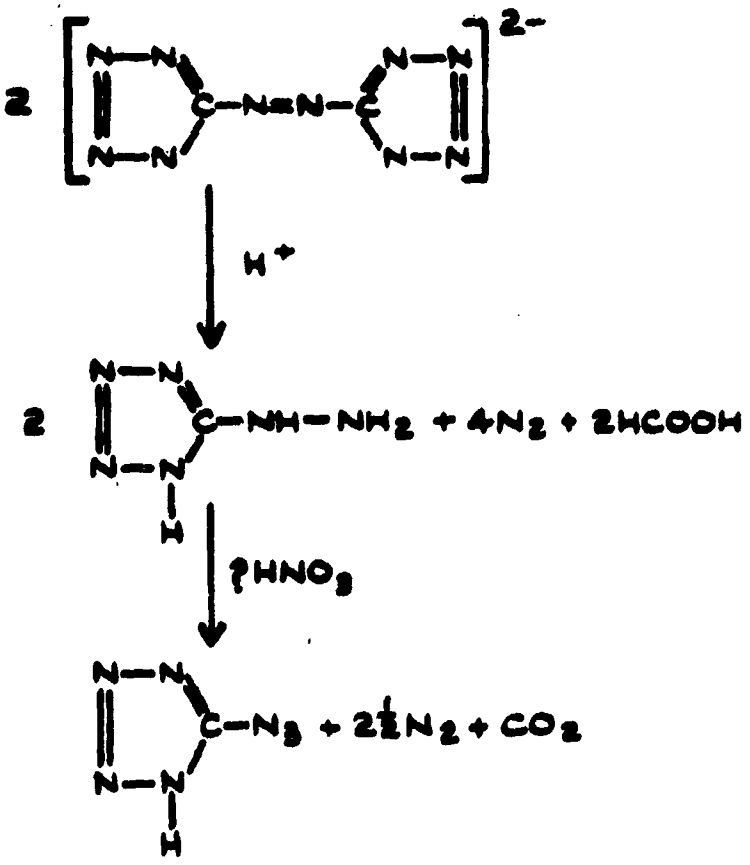
4 2 2 Possible Mechanism of the Reaction

Although little has been done in this respect the overall mechanism can be postulated with the help of results of the gas analysis and some experiments with 5-hydrazinotetrazole.

When disodium azotetrazole pentahydrate ($Na_2AT.5H_2O$) was treated with an excess of dilute nitric acid, gas was evolved for approximately 30 min by which time the solution was colourless. The volume of gas corresponded approximately to four moles rather than the seven expected if complete destruction occurred as shown below.



It is important that only one half a mole of carbon dioxide was obtained per mole of azotetrazole destroyed. If it is assumed that the first step in the reaction is the same as that for hydrochloric and sulphuric acids, ie the formation of 5-hydrazinotetrazole, nitrogen and formic acid, then it follows that two molecules of the hydrazine must react to form one of the 5-azidotetrazole as shown below.



$\therefore$ Total gas/mole azotetrazole $= 3\frac{1}{4}N_2 + \frac{1}{2}CO_2$

The elements of 5-azidotetrazole were shown to be in the resulting solution from the nitric acid destruction of azotetrazole by first treating the solution as above and evaporating to dryness to remove any formic acid. This residue was taken up in water and reacted with acidified ceric ammonium nitrate to give a gas mixture whose analysis corresponded to that required for 5-azidotetrazole.

It has also been shown that 5-hydrazinotetrazole will react with warm dilute nitric acid to give 5-azidotetrazole which was isolated as the silver salt. A spontaneous explosion occurred on trying to dehydrate the reaction mixture over P_2O_5.

The nature of the reaction between the two moles of the hydrazine to give 5-azidotetrazole has not been resolved but two possible mechanisms are suggested by the results. The first involves reduction of nitric acid by some of the hydrazine to give nitrous acid which then reacts with the remaining hydrazine to give 5-azidotetrazole. The second mechanism involves two moles of the hydrazine coupling, possibly via the diazonium salt, to give a tetrazene which then decomposes to the azide and gaseous products. It is not in the scope of this Note to elucidate the mechanism but it would be of interest to do so in the future.

5 ACKNOWLEDGEMENTS

We are greatly indebted to Messrs Duke, Mullenger, Paul, Farey and Miss Best of SGC for the analytical and X-ray powder pattern results and to members of the Sensitiveness Section for sensitiveness and hazard evaluation.

6 REFERENCES

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2	Taylor G W C, Thomas A T, Williams R J E	UNPUBLISHED BRITISH REPORT
3		Brit Pat 185,555 (June 27 1921)
4	Thiele J	Annalen 1898, 303, 57
5	Thiele J, Ingle H	Annalen 1895, 287, 233
6	Lieber E, Levering D R	J Amer Chem Soc 1951, 73, 1313
7	Feigl F	Spot Tests in Organic Analysis, Elsevier 7th Edition 1966, pp 451
8	Thiele J, Marais J T	Annalen 1892, 273, 144

Most of the solid products of the reactions described in Section 2 of this Note have been identified by their infrared spectra. The spectra were obtained from KBr discs.

Experimental

A vibration mill with a steel capsule and steel balls was used to mix the samples with the potassium bromide. The spectroscopic grade potassium bromide was ground to 200 mesh and dried at 120°C for 24 h. A 13 mm diameter evacuable die and a hydraulic press were used to form the disc and a Perkin Elmer 257 spectrophotometer was used to record the spectra.

Method

The samples were weighed (1 to 4 mg) and added to a measured quantity (about 0.4 g) of KBr contained in the mill capsule. The capsule was stoppered and after pre-mixing by hand was vibrated for 3 minutes. Half of the mixture was used to make a disc, 10 tonnes pressure being applied for 1 min after evacuating the die for 3 minutes. The remaining mixture was used if the first disc was faulty or too concentrated.

Hypersensitive materials

The 5-azidotetrazoles were too sensitive to dry and weigh so the above procedure was modified. The water over the precipitate was replaced by ethanol and a quantity of the ethanol (suspension) estimated to contain 1 or 2 mg of sample was transferred using a polythene spatula to a capsule containing the KBr. The capsule was placed in an oven at 70°C for 2 hours, then milled and pressed as above. It was found that the hypersensitive 5-azidotetrazoles could be milled with KBr and pressed and twenty samples were processed without incident.

Infrared Spectra

There was some difficulty initially in identifying the 5-azidotetrazole compounds; the only reference spectra were published in 1951 and were run as paraffin mulls on a single beam spectrometer. The paraffin peaks mask two of the three major 5-azidotetrazole peaks.

The reference compounds described in Section 2 of the report were made and the infrared spectra recorded. The reference spectra obtained are shown in Spectra 1 - 9.

KEY TO SPECTRA

Fig 1 Disodium 5-azotetrazole pentahydrate ($Na_2AT.5H_2O$)

2 Monobasic lead azotetrazole ($PbAT.Pb(OH)_2$) (RD 1355)

3 Silver azotetrazole

4 5-Hydrazinotetrazole

5 " monohydrochloride

6 " hydrochloride intermediate

7 " benzal

8 5-Azidotetrazole

9 Silver 5-azidotetrazole

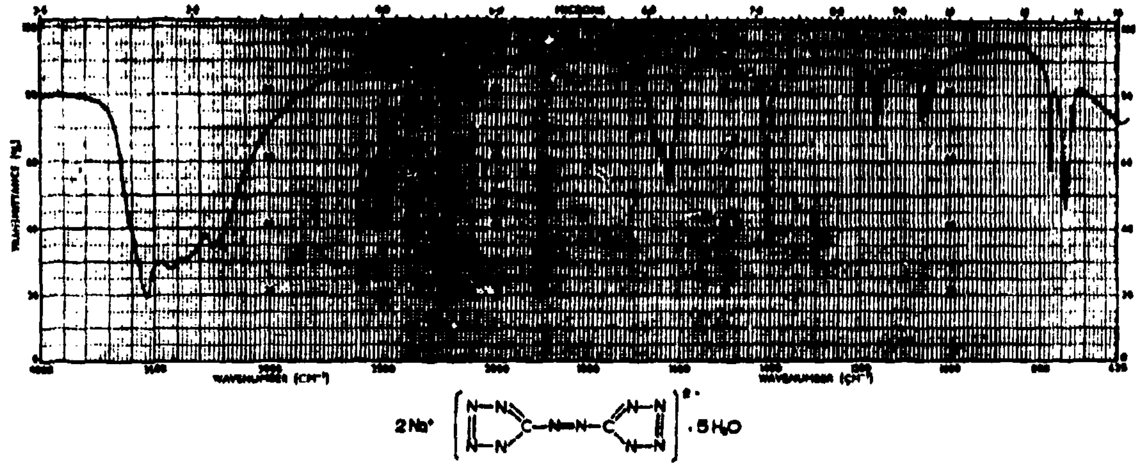

FIG. 1

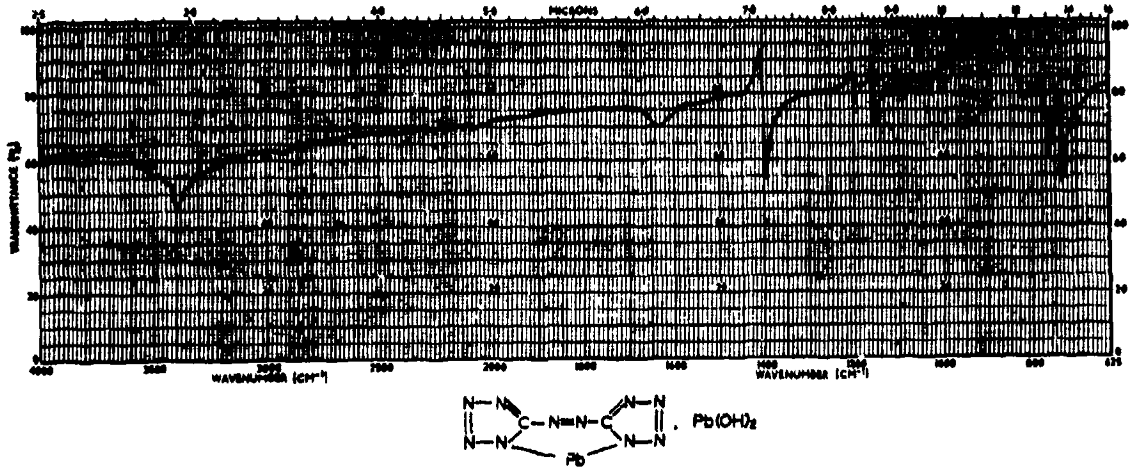

FIG. 2

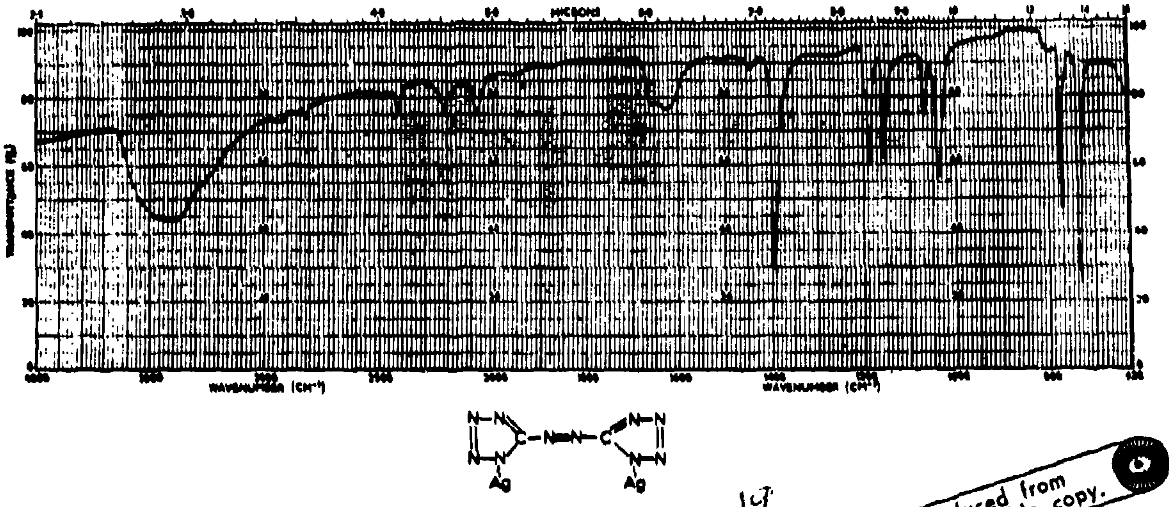

FIG. 3

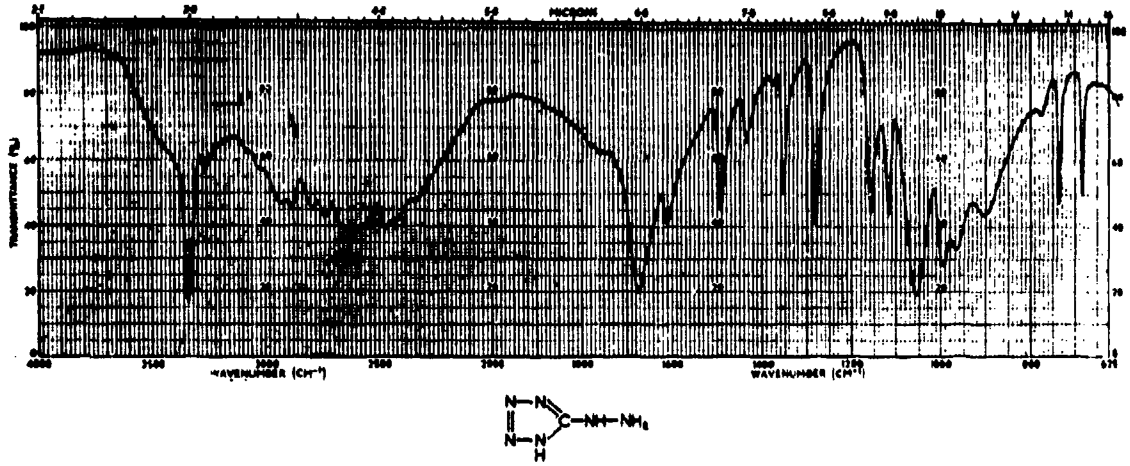

FIG. 4

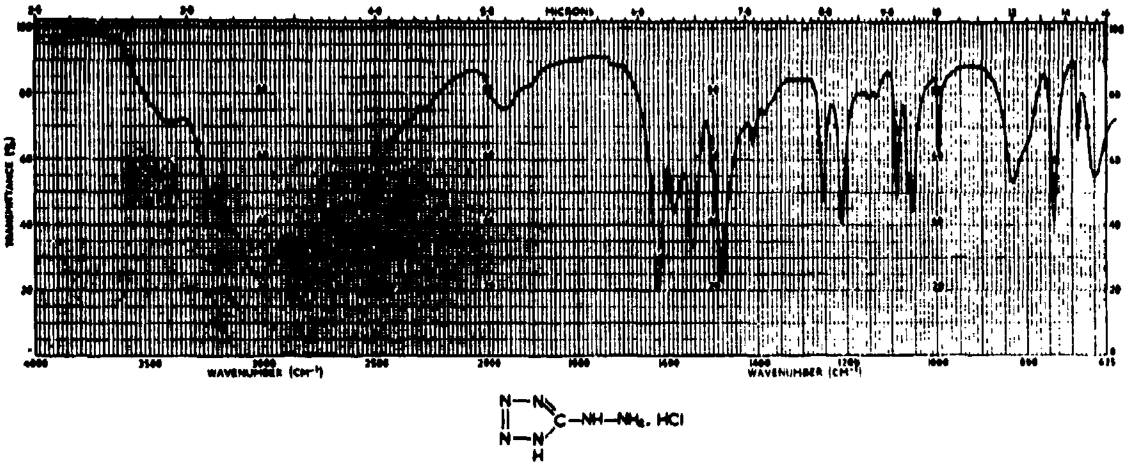

FIG. 5

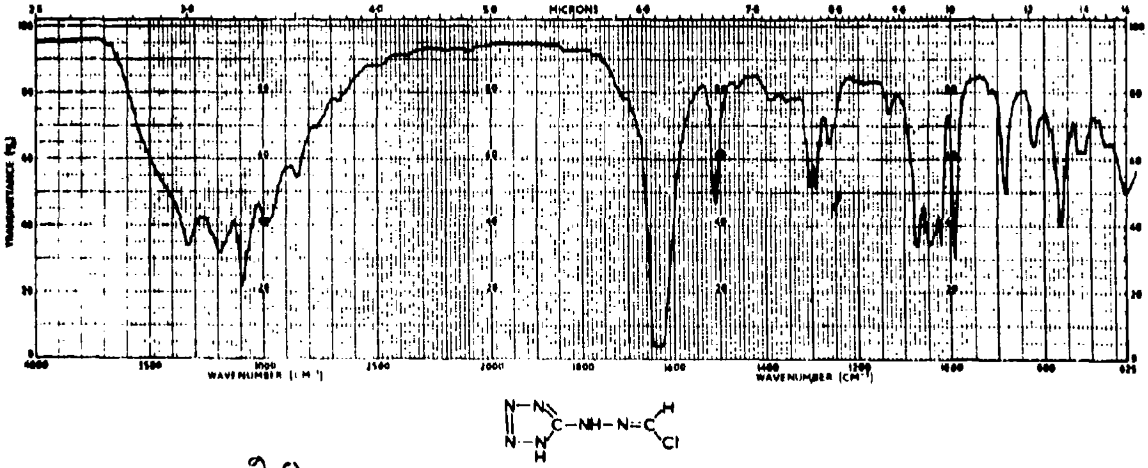

FIG. 6

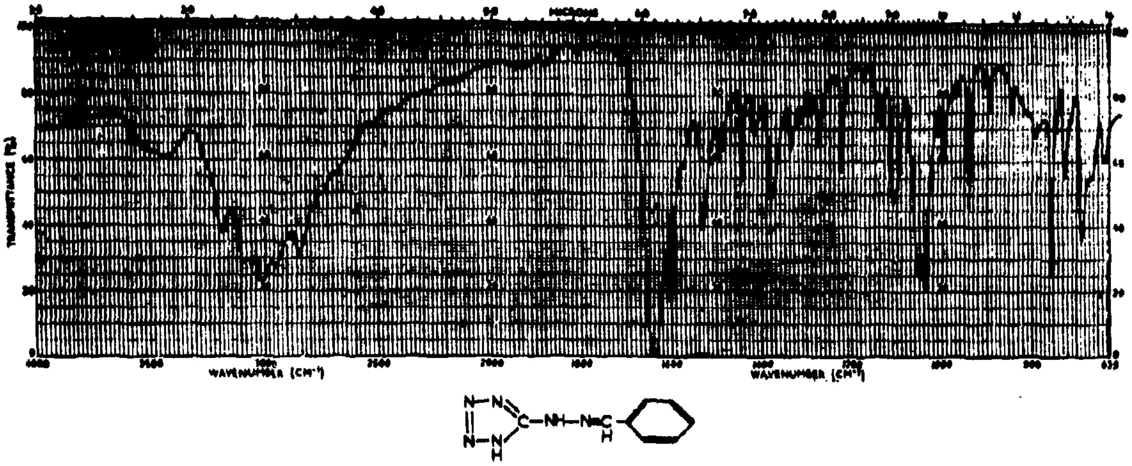

FIG. 7

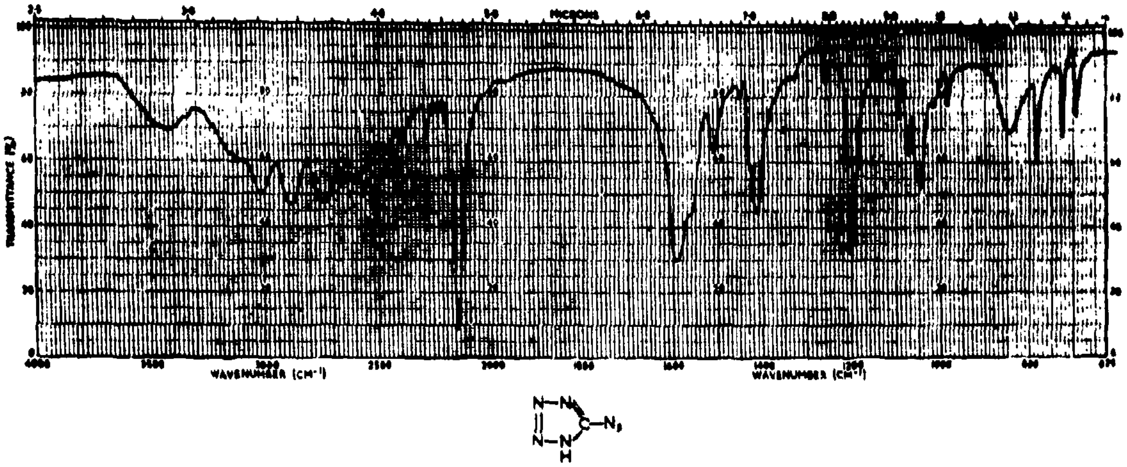

FIG. 8

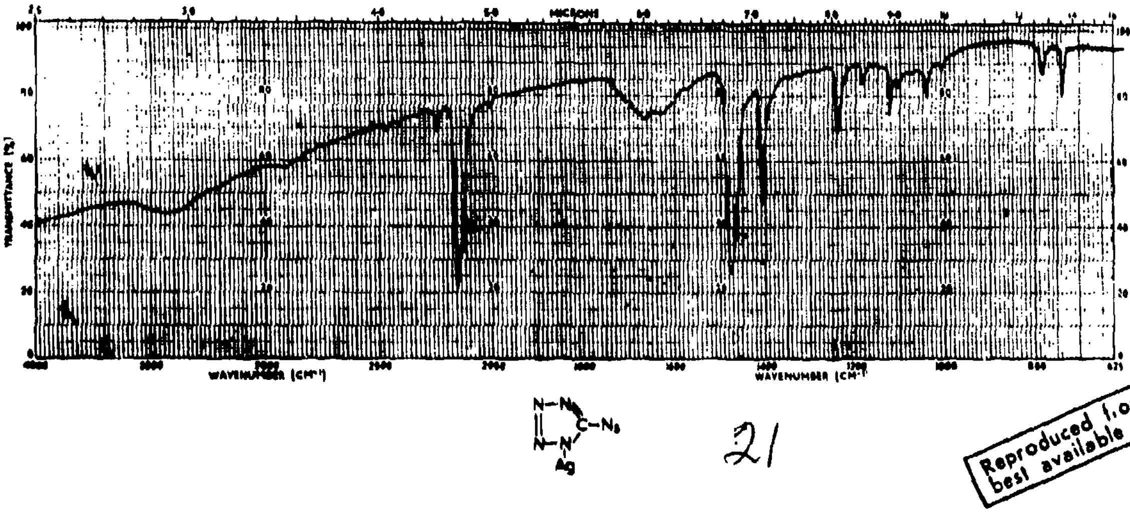

FIG. 9