Nitramines and Nitramides. Part VII. The Irreversible Decomposition of Nitroguanidine and of Nitrourea by Sulphuric Acid.*

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The decomposition of nitroguanidine and of nitrourea by means of sulphuric acid at 55° has been investigated quantitatively. It appears that nitroguanidine (I) is converted into urea (II). The final products depend, however, upon the concentration of the sulphuric acid, since nitric acid and the urea formed from nitroguanidine may be removed by combination and the subsequent decomposition of nitrourea. In this event the major end-product is guanidine. The behaviour of nitrourea (investigated separately) correlates well with, and elucidates, the behaviour of nitroguanidine.

MENTION has already been made (Part V, *J.*, 1953, 3341) of the irreversible decomposition of certain *N*-nitro-compounds in sulphuric acid–water media. The behaviour of nitroguanidine and of nitrourea has now been examined, in acid of 83·6—99·3% w/w concentration, at a temperature (55°) sufficiently high to produce complete decomposition in a reasonable period. The solutions, initially 0·2M, were made from guanidine and urea nitrates respectively. Since the nitration–denitration equilibrium was established rapidly in the conditions employed, this procedure was equivalent to the use of nitroguanidine or nitrourea as initial materials.

It was found that urea, guanidine (added as guanidine sulphate), and nitric acid (added as ammonium nitrate) were unaffected by treatment which brought about, in the same time, complete decomposition of guanidine nitrate and *ca.* 75% decomposition of urea nitrate. The decomposition of the latter substances must therefore occur through the *N*-nitro-compounds.

The reaction may be formulated (without, for the moment, any implication regarding the precise mechanism) as the hydrolysis $X{\cdot}NH{\cdot}NO_2 + H_2O \longrightarrow X{\cdot}OH + NH_2{\cdot}NO_2$. It may be admitted that no direct evidence of the formation of nitramine has been obtained; but a colourless gas was evolved during the decompositions, and we found that the addition of nitramine to 99·3% w/w sulphuric acid at 5° led to effervescence and a residual solution containing a negligible quantity of nitric acid. Davis (*J. Amer. Chem. Soc.*, 1922, **44**, 868) has shown that (at higher temperatures) in the Kjeldahl process nitroguanidine reacts according to the equation $NH_2{\cdot}C(NH){\cdot}NH{\cdot}NO_2 + H_2O \longrightarrow CO_2 + N_2O + 2NH_3$; he also (Davis and Blanchard, *ibid.*, 1929, **51**, 1790) claimed the isolation of nitramine from a concentrated solution of nitrourea in sulphuric acid.

It appears that, in the conditions we used, nitroguanidine (I) is converted (reaction *A*) into urea (II). The formation of urea was first postulated on theoretical grounds, then confirmed by quantitative determination with urease, and finally proved by isolation of the xanthhydrol derivative. Since the nitroguanidine is at the same time in equilibrium with guanidine nitrate (reaction *B*), the urea formed in (*A*) is converted (reaction *C*) in part into nitrourea (III). This, in turn, suffers irreversible decomposition, presumably into carbamic acid and nitramine (reaction *D*). The end products are probably carbon dioxide and ammonium sulphate, formed either directly or by way of cyanic acid. We found that com-

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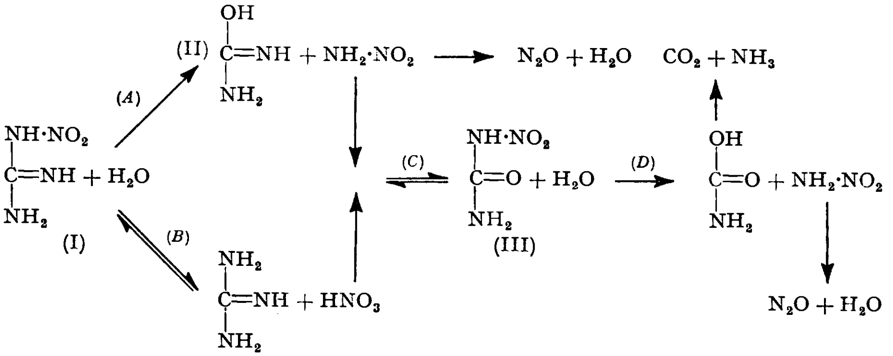
* Part VI, *J.*, 1953, 3349.

plete decomposition of nitrourea by sulphuric acid yielded one molecular proportion of ammonia when the reaction mixture was made alkaline and distilled.

During the decomposition of nitroguanidine we determined the total nitric acid (free, and bound as $>N\cdot NO_2$), free nitric acid, guanidine, and urea. In 99·3% w/w sulphuric acid, the amounts of total nitric acid, free nitric acid, and guanidine fell, whilst the urea content rose to, finally, a 75% yield. In 88·1 and 83·6% w/w sulphuric acid, total and free nitric acid concentrations fell, whilst that of urea rose only to 11 and 5% yields, respectively; guanidine (43 and 46% yields, respectively) was the major product.



The facts reported in the preceding paragraph correlate well with the behaviour of urea. Urea nitrate (equivalent, in sulphuric acid, to nitrourea) was found to be almost stable in 99·3% w/w sulphuric acid at 55° : the decomposition is much slower than that of guanidine nitrate. It follows that, for guanidine nitrate under these conditions, most of the nitric acid is removed by reactions *B* and *A*, and very little by reactions *C* and *D*; and, as found experimentally, urea is the major product. In 88·1 or 83·6% w/w sulphuric acid we found the decomposition of urea nitrate to be much faster than that of guanidine nitrate. Therefore, for guanidine nitrate under these conditions, there is also considerable loss of nitric acid by reactions *C* and *D*; the supply of nitric acid runs out, leaving some guanidine behind. In 88·1 and 83·6% w/w sulphuric acid equilibrium *B* lies mainly to the left, and the rise in free guanidine content must be due to denitration of (I) as the reactions proceed. The relatively slow decomposition of urea nitrate in 99·3% w/w sulphuric acid is in part—but probably not wholly, as analysis of the results already presented (Part V, *loc. cit.*) shows—due to the fact that equilibrium *C* lies almost completely to the left. Such a solution contains very little nitrourea which can suffer decomposition.

The observed yield (46%) of guanidine obtained by complete irreversible decomposition of nitroguanidine (in 83·6% w/w sulphuric acid) is in fact high. Loss of nitric acid by reactions *C* and *D* can only occur after urea has been formed, and nitric acid lost, by reaction *A* : the maximum possible yield of guanidine on the basis of these equations is 50%.

We have made similar measurements in 94·7% w/w sulphuric acid. These show that this concentration is approximately the boundary between predominance of the route yielding urea, and the route yielding guanidine.

It may be added that (i) the yields obtained from nitroguanidine are not fully quantitative, especially in sulphuric acid of >90% w/w concentration, and therefore some minor reactions are possibly undiscovered; and (ii) the fall in free nitric acid concentration, in the case of nitrourea, is approximately of the second order—a result consonant with a decomposition of the first order with respect to nitrourea. These observations are dealt with more fully in the Experimental section.

EXPERIMENTAL

The solutions were made up, and analysed for free nitric acid in the presence of *N*-nitro-compounds, in the manner previously described (Part V, *loc. cit.*; Simkins and Williams, *J.*, 1952, 3086). Times (*t*, in min.) were measured from the initial mixing, and the solutions were made up with acid previously warmed to 55°. The sampling pipettes were calibrated by weight delivered at 55°, and all molarities reported are those which would have occurred in the solution after sudden cooling, without chemical change, to 25°. Owing to thermal expansion, the true molarities at 55° must have been slightly smaller.

" Total " Nitric Acid.—A 3-ml. sample was pipetted into 98% sulphuric acid (100 ml.) in a 250-ml. wide-mouthed flask, and titrated directly with ferrous ammonium sulphate (*ca.* 0·07N in 30% sulphuric acid) to a potentiometric end-point, under an atmosphere of carbon dioxide (Treadwell and Vontobel, *Helv. Chim. Acta*, 1937, **20**, 573; and especially Cottrell, MacInnes, and Paterson, *Analyst*, 1946, **71**, 207). We used the apparatus of Cottrell *et al.* (*loc. cit.*), who found that nitroguanidine thus liberated nitric acid quantitatively; and we found nitrourea to behave in the same way. The analysis was accurate to ±0·0005M-nitric acid.

Guanidine.—A 5-ml. sample was pipetted into 175 ml. of a stock solution of picric acid (1·960 g./l.; saturated with guanidine picrate at 0°). Sodium hydroxide (10 ml. of 50%, w/w) was added, and the partly neutralised solution kept overnight in an ice-chest. Aqueous guanidine carbonate (1 ml. of concentration 7·203 g./l.) was then added to form nuclei, and the precipitation completed by stirring at 0° for 30 min. The precipitate was collected in a sintered-glass crucible, washed with ice-cold water (50 ml.; saturated with guanidine picrate at 0°), and dried in a steam-oven. Simpler methods, and the use of ammonium picrate solutions, were found to be inapplicable on account of the relatively large initial quantity of sulphuric acid. A variable empirical correction, related to the weight of guanidine picrate precipitated, was necessary on account of (*a*) the solubility of guanidine picrate, and (*b*) the addition of guanidine carbonate (equiv. to 23 mg. of picrate) to seed the solution. Our correction graph was based on the following figures (in each case the observed weight of precipitate in mg. is followed by the net correction in mg.): 242, 23; 197, 11; 147, 3; 91, 1; 39, −4; 4, −4. The analysis was accurate to ±0·002M-guanidine.

Urea.—A 3-ml. sample, pipetted into water (20 ml.), was made slightly alkaline with sodium hydroxide solution (50% w/w) and finally neutralised with 0·05N-hydrochloric acid, a mixed methyl-red–bromocresol-green indicator being used. Three 25-mg. tablets of urease (Hynson, Westcolt, and Dunning) were ground in water (5 ml.), neutralised (hydrochloric acid and mixed indicator), and added to the urea solution. The liberated ammonium carbonate was titrated from time to time during incubation (20 min. at 45°), and complete decomposition was assured by setting the stoppered flask aside overnight at 45° before the final addition of hydrochloric acid was made. The analysis was accurate to ±0·001M-urea.

Rapidity of Equilibrium at 55°.—Solutions (0·2M) were made up in 83·6% w/w sulphuric acid at 55°, and free nitric acid was determined *t* min. after mixture with the following results: guanidine nitrate, $t = 9$, $HNO_3 = 0{\cdot}032$M; nitroguanidine, $t = 9$, $HNO_3 = 0{\cdot}031$M; urea nitrate, $t = 10$, $HNO_3 = 0{\cdot}107$M; nitrourea, $t = 9$, $HNO_3 = 0{\cdot}102$M. In the urea experiments considerable decomposition (see Expt. 8) has already occurred, but the approximate agreement indicates that the speed of equilibration does not seriously influence the observed course of decomposition. In more concentrated acid equilibrium is established even more rapidly.

Decomposition of Guanidine Nitrate and of Urea Nitrate.—The principal results are recorded in Tables 1 and 2.

Stability of Urea, Guanidine, and Nitric Acid in 99·3% *w/w Sulphuric Acid at* 55°.—Separate solutions of urea, guanidine sulphate, and ammonium nitrate (all 0·2M) were made up; urea, guanidine, and free nitric acid were, respectively, found to be invariant (0·2M to within experimental error) up to 48 hr. Davis and Abrams (*J. Amer. Chem. Soc.*, 1925, **47**, 1043) suggest that, at high temperatures, ammonium nitrate is decomposed by sulphuric acid to yield (*via* nitramine) nitrous oxide and water; no sign of such a reaction was found at 55°.

Decomposition of Nitramine in 99·3% *w/w Sulphuric Acid.*—Nitramine (sufficient to make a 0·2M-solution) was added portionwise to the acid at 0° to 5°. Vigorous effervescence occurred, and the residual solution was only 0·003M in free or total nitric acid. This small quantity may well have come from nitrourethane, a possible impurity in samples of nitramine.

Isolation of the Xanthhydrol Derivative of Urea.—A 2M-solution of guanidine nitrate in 99·3% w/w sulphuric acid was kept for 24 hr. at 55°. A sample (1 ml.) was diluted with water (5 ml.) and cooled; subsequent addition of glacial acetic acid (3·5 ml.) and xanthhydrol (5 ml. of 10% solution in methyl alcohol) gave a precipitate which was collected, washed with methyl alcohol, and dried; it had m. p. 273°, not depressed by mixture with the authentic urea derivative.

Analysis of the Yields of Guanidine and Urea in Relation to the Fall in Nitric Acid Concentration.—On the basis of the equations presented, nitric acid can only be removed from the solutions through decomposition of nitroguanidine and/or nitrourea: each molecule of potential nitric acid which disappears removes at the same time one potential guanidine or urea molecule. The

TABLE 1. *Decomposition of guanidine nitrate* (0·2M *at* 25°) *in sulphuric acid–water mixtures at* 55° ± 0·2°.

	Total $[HNO_3]$		Free $[HNO_3]$		[Guanidine]		[Urea]	
	t (min.)	M	*t* (min.)	M	*t* (min.)	M	*t* (min.)	M
Expt. 1. H_2SO_4, 99·3%, w/w.	50	0·138	14	0·143	25	0·138	30	0·039
	97	0·108	75	0·104	83	0·100	91	0·081
	204	0·071	183	0·066	191	0·069	197	0·113
	300	0·053	275	0·051	285	0·055	292	0·126
	405	0·040	388	0·038	394	0·043	400	0·134
	638	0·025	619	0·023	626	0·029	632	0·143
	1,393	0·008	1,369	0·007	1,378	0·019	1,384	0·149
	2,815	Nil	2,830	Nil	2,838	0·013	2,845	0·151
Expt. 3. H_2SO_4, 94·7%, w/w.	34	0·163	11	0·068	16	0·065	27	0·024
	87	0·112	64	0·051	73	0·060	80	0·049
	188	0·050	173	0·023	178	0·059	182	0·065
	281	0·023	262	0·011	269	0·058	275	0·068
	393	0·010	370	0·004	379	0·056	386	0·071
	1,440	Nil	1,446	Nil	1,450	0·054	1,457	0·072
Expt. 5. H_2SO_4, 88·1%, w/w.	28	0·189	13	0·018	21	0·017	18	0·004
	85	0·162	68	0·014	77	0·021	73	0·008
	206	0·116	183	0·007	198	0·035	189	0·011
	291	0·092	271	0·004	284	0·043	277	0·014
	411	0·066	392	0·001	404	0·049	397	0·018
	763	0·015	741	Nil	757	0·073	750	0·019
	1,622	0·002	1,495	Nil	1,509	0·085	1,501	0·022
Expt. 7. H_2SO_4, 83·6%, w/w.	38	0·196	16	0·031	25	0·029	28	0·003
	91	0·188	70	0·029	76	0·031	82	0·004
	268	0·164	241	0·023	250	0·035	258	0·005
	634	0·123	613	0·013	622	0·045	629	0·006
	1,357	0·069	1,330	0·005	1,340	0·064	1,350	0·008
	2,071	0·039	2,045	0·002	2,055	0·075	2,064	0·009
	4,253	0·007	4,224	Nil	4,234	0·090	4,243	0·010
	10,080	Nil	10,032	Nil	10,041	0·092	10,054	0·010

TABLE 2. *Decomposition of urea nitrate* (0·2M *at* 25°) *in sulphuric acid–water mixtures at* 55° ± 0·2°.

	Total $[HNO_3]$		Free $[HNO_3]$		[Urea]	
	t (min.)	M	*t* (min.)	M	*t* (min.)	M
Expt. 2. H_2SO_4, 99·3%, w/w.	25	0·193	14	0·192	18	0·193
	67	0·186	56	0·185	62	0·185
	190	0·168	163	0·169	172	0·165
	548	0·132	532	0·131	537	0·131
	1,382	0·091	1,360	0·091	1,370	0·093
	2,933	0·059	2,902	0·058	2,908	0·058
	4,493	0·043	4,475	0·041	4,483	0·043
Expt. 4. H_2SO_4, 94·7%, w/w.	19	0·139	10	0·156	14	0·150
	78	0·072	48	0·092	60	0·087
	133	0·050	111	0·055	119	0·056
	199	0·037	187	0·038	193	0·040
	398	0·020	386	0·020	392	0·023
	1,205	0·006	1,190	0·006	1,198	0·010
Expt. 6. H_2SO_4, 88·1%, w/w.	27	0·038	18	0·045	10	0·071
	58	0·017	50	0·017	43	0·026
	190	0·004	182	0·004	173	0·008
Expt. 8. H_2SO_4, 83·6%, w/w.	26	0·097	14	0·095	10	0·107
	49	0·048	43	0·048	37	0·058
	84	0·030	77	0·030	72	0·032
	157	0·016	152	0·015	146	0·017
	218	0·011	211	0·011	198	0·013

relation appears to be quantitative in the case of urea nitrate; the curves for free nitric acid and for urea are identical, showing that the removal of nitric acid does not either lag behind or precede the removal of urea; and therefore, apart from the unlikely contingency of two unknown reactions whose effects cancel each other, the decomposition products of nitrourea cannot react significantly with urea or nitric acid.

This is not the case with guanidine nitrate, even when allowance is made for the behaviour of the urea formed. It is possible, at the end of the decomposition, when no significant proportion of the materials in question is " hidden " as *N*-nitro-compounds, to determine how much potential guanidine and potential urea have been destroyed. The sum of these should be the same as the total fall in nitric acid concentration, but is in fact smaller (Table 3). The difference of up to 12% seems much greater than possible errors in analysis, and presumably indicates the extent of side reactions.

TABLE 3. *Comparison of nitroguanidine and nitrourea decomposed with observed loss of nitric acid, for guanidine nitrate* (0·2M *at* 25°) *in sulphuric acid at* 55°. (*All values expressed as molarities at* 25°, *and calculated from observations made when decomposition was essentially complete.*)

	Sulphuric acid, % w/w.			
	99·3	94·7	88·1	83·6
Time of decomposition, hr.	47	24	25	167
A. Nitroguanidine decompd. = (0·2 − residual guanidine) = urea formed	0·187	0·146	0·115	0·108
B. Nitrourea decompd. = (urea formed − residual urea)	0·036	0·074	0·093	0·098
C. Theoretical loss of nitric acid (A + B)	0·223	0·220	0·208	0·206
D. Observed loss of nitric acid	0·200	0·200	0·198	0·200

Rate of Decomposition of Nitrourea.—When slow enough for accurate measurement, the rate was of the second order. From the equilibrium constant, [Nitrourea][H_2O]/[Urea][HNO_3], and the fact that, even in 99% acid, [H_2O] is essentially constant during the decomposition of 0·2M-urea nitrate, [Nitrourea] $\propto$ [Urea][HNO_3]. Since urea and nitric acid were initially present in equimolar quantities, and if these disappear only through the decomposition of nitrourea, with elimination of equivalent quantities of bound urea and bound nitric acid, then [Urea] = [HNO_3] at any stage; and [Nitrourea] $\propto$ [HNO_3]^2. Counter-balancing side reactions are possible, but unlikely; the second-order fall of free nitric acid content supports the hypothesis of decomposition through the *N*-nitro-compound, and suggests a first-order rate with respect to nitrourea.

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