283. *The Nitration of Guanidine in Sulphuric Acid. Part II.* Kinetics of* N-*Nitration of the Guanidinium Ion and Denitration of Nitroguanidine.*

By Gwyn Williams and R. J. J. Simkins.

The conversion of guanidinium ion into nitroguanidine and the reverse denitration of nitroguanidine have measurable speeds in 71·5—83% sulphuric acid. In a given medium the rate of *N*-nitration is proportional to guanidinium ion and nitric acid concentrations, and it falls very sharply with increasing water content of the medium. Correlation of nitration speeds with the influence of medium upon the ionisation of triarylmethanol indicators suggests that the nitrating agent is the nitronium ion. In a given medium, the nitration velocity coefficient is reduced by increased initial concentration of guanidinium salt or of added inorganic salts. The reduction may be due largely to decreasing conversion of nitric acid into nitronium ion.

The rate of denitration of nitroguanidine is best represented as being proportional to nitroguanidine concentration; it falls with decreasing acidity of the medium, but less sharply than does the rate of nitration.

The transformation of guanidine nitrate into nitroguanidine in sulphuric acid is reversible (Simkins and Williams, Part I, *loc. cit.*; Holstead and Lamberton, *J.*, 1952, 1886). The overall conversion into uncharged nitroguanidine (obtained by precipitating the product in water) is given by equation (1);† but the reaction in sulphuric acid should probably be represented by equation (2), in which the symbols G and P stand for the uncharged guanidine and nitroguanidine molecules, respectively.

$$ {}^{+}H_2N{:}C(NH_2)_2\}NO_3^- = HN{:}C(NH_2){\cdot}NH{\cdot}NO_2 + H_2O \quad . \ . \ . \ . \ . \ . \quad (1) $$

$$ GH^+ + NO_2^+ + HSO_4^- \rightleftharpoons PH^+ + H_2SO_4 \quad . \ . \ . \ . \ . \ . \ . \quad (2) $$

Evidence is given below for the assumption that the nitronium ion is the nitrating agent.

In media containing more than 85% of sulphuric acid, the equilibrium between guanidine nitrate and nitroguanidine is established too quickly for the reaction rates to be measured (Part I, *loc. cit.*);‡ but, in the medium range 71·5—83% sulphuric acid, the

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* Part I, *J.*, 1952, 3086.

† In neutral nitroguanidine the nitro-group is possibly attached to the imino-nitrogen atom (Barton, Hall, and Wright, *J. Amer. Chem. Soc.*, 1951, **73**, 2201); but, as pointed out in Part I, the distinction is unimportant for sulphuric acid solution, in which the compound is present as nitroguanidinium ion.

‡ With high concentrations of guanidine nitrate (*e.g.*, 1M), the slow dissolution of the starting material in the medium causes an apparently slow conversion; but the actual chemical reaction is fast.

approach to equilibrium, from either side, proceeds at a measurable rate. The choice of correct kinetic equations is assisted by the examination of the initial stages of the nitration and denitration processes, the reverse reaction then obtruding itself least.

N-*Nitration of the Guanidinium Ion.*—In order to vary the guanidine and nitric acid concentrations independently, guanidine carbonate has been used, as starting material, instead of guanidine nitrate; and the rate of approach from the left-hand side to equilibrium, in the reversible system (2), has been measured, in 71·5—83% sulphuric acid media, by dissolving guanidine carbonate in the given medium, mixing the solution with a solution of anhydrous nitric acid in the same medium, and following the fall of nitric acid concentration with time.

In these media, the empirical equilibrium products [*K* in Part I; cf. equation (5) below] lie well below the maximum value which they assume in about 88% sulphuric acid; but with the concentrations employed the equilibrium end-points generally correspond to 60—95% conversion of the initial reagent present in defect into nitroguanidine. Consequently, the initial stage of nitration may often be considered to be relatively little disturbed by the reverse reaction.

When $1/[HNO_3)$ (*e.g.*, in expt. 204) or log $\{[HNO_3]/[GH^+]\}$ (*e.g.*, in expts. 210, 211) (according to whether the initial reactant concentrations are equivalent or not) is plotted against time, the plot is initially linear, as shown in Figs. 1 and 2, whereas graphs of log $[HNO_3]$ against time are initially curved. This circumstance suggests that equation (3) is valid for the nitration process.

FIG. 1.

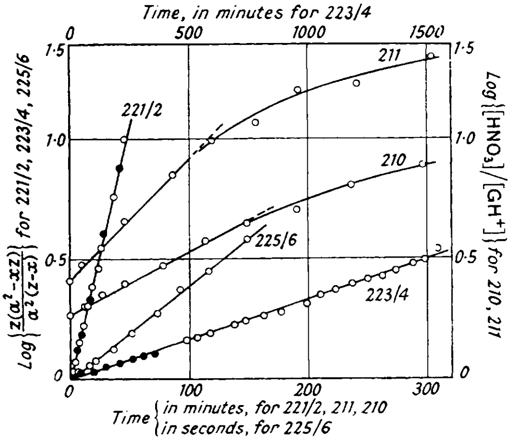
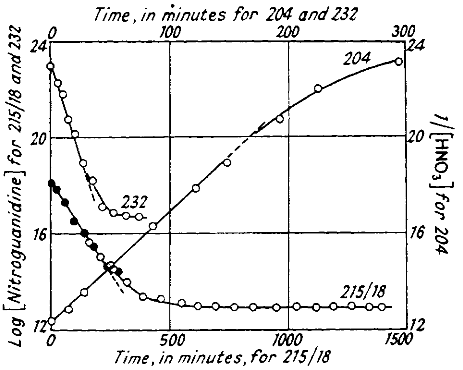


FIG. 2.



$$- d[HNO_3]/dt = k_2[HNO_3][GH^+] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Here, and elsewhere, $[HNO_3]$ denotes the analytically determined total concentration of nitric acid.

Influence of Initial Reagent Concentrations.—The results given in Table 1 (a) for velocity coefficients, k_2, derived graphically from equation (3) for the initial stages of nitration (cf. Fig. 2), show that k_2 changes little for a 13-fold variation of initial nitric acid concentration. The rate of *N*-nitration is thus nearly strictly proportional to nitric acid concentration, in accordance with equation (3).

On the other hand, the coefficient k_2, of equation (3), falls substantially with rising initial concentration of guanidinium ion [Table 1 (b)], though k_2 is not inversely proportional to initial $[GH^+]$. This result is not necessarily inconsistent with equation (3), because there is some evidence (see p. 1391) that variation of guanidinium salt concentration alters the acidity of the system to a sufficient extent to account for the variation of k_2 shown in Table 1 (b). When both reagent concentrations are varied in such a way that they are always equivalent, k_2 does not change greatly [Table 1 (c)].

Denitration of Nitroguanidine.—In experiments with nitroguanidine as starting material, not more than about 30% denitration occurs (in reasonable time; in the least acid media, equilibrium is approached very slowly). The initial stages of the denitration reactions (followed by measuring the rise of nitric acid concentration with time) therefore correspond to very small extents of conversion of nitroguanidine; and initial rates of denitration (to be as free as possible from the opposing nitration reaction) cannot be measured very accurately.

For the initial stage of each reaction the plot of log [nitroguanidine] against time is approximately linear (Fig. 2, expts. 232, 215/18), in accordance with equation (4) :

$$-\,d[PH^+]/dt = k_1[PH^+] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

However, the reasonable range of validity of each plot in Fig. 2 extends over so small a conversion range that the linear graph is far from reliable as a test of equation (4). Nevertheless, when the initial concentration of nitroguanidine is increased 8-fold, in a given medium, the time taken for 5% denitration changes (and, in fact, *rises*) by not more than 50% (see col. 4, Table 2). Equation (4) seems, therefore, to be the best simple expression for the rate of denitration, with the reservation that k_1 (calculated from the linear graphs of Fig. 2) falls slowly with rising initial concentration of nitroguanidine in a given medium. In considering this " concentration variation " of k_1, it is to be recalled that the introduction of varying concentrations of the base nitroguanidine must alter the acidity of the system to different extents. As shown in Table 2, k_1 falls with decreasing acidity of the medium.

TABLE 1.

Medium, % H_2SO_4	Expt. no.	Initial concn., M : Guanidine	Initial concn., M : HNO_3	$100k_2$, min.$^{-1}$	$100k_2'$	Medium, % H_2SO_4	Expt. no.	Initial concn., M : Guanidine	Initial concn., M : HNO_3	$100k_2$, min.$^{-1}$	$100k_2'$
(a) *Variation of initial nitric acid concentration at 25°.*											
75·47	206	0·2024	0·0509	3·56	—	—	208	0·2026	0·2446	3·73	—
	203	0·2025	0·0815	3·62	—		209	0·2019	0·2974	3·79	—
	202	0·2027	0·0996	3·55	3·62		210	0·2022	0·3744	3·59	—
	198	0·2020	0·1481	3·60	—		211	0·2019	0·5190	3·60	—
	190	0·2025	0·2037	3·60	4·10		212	0·2023	0·6649	3·91	—
(b) *Variation of initial guanidine concentration at 25°.*											
81·14	162/3	0·0957	0·1923	369	374		179/0	0·2951	0·1997	15·2	(15·6)
	160/1	0·1907	0·1930	209	259						
	164/5	0·3822	0·1923	158	161	75·47	194	0·0508	0·2028	6·52	6·91
							193	0·1013	0·2037	5·02	6·07
78·33	182/3	0·0494	0·1988	25·4	27·2		192	0·1525	0·2030	4·36	(4·84)
	177/8	0·0987	0·1990	23·0	24·1		190	0·2025	0·2037	3·60	4·10
	181	0·1486	0·1985	18·5	22·8		191	0·3034	0·2040	2·85	(3·66)
	175/6	0·1979	0·1985	18·9	(17·1)						
(c) *Equivalent reagent concentrations : variation of medium at 25°.*											
82·94	225/6	0·2004	0·2023	995	1100	75·47	205	0·0506	0·0509	4·15	—
							204	0·0813	0·0812	4·44	—
81·14	160/1	0·1907	0·1930	209	259		201	0·0993	0·0994	4·26	—
							200	0·1329	0·1331	4·07	—
79·24	221/2	0·2070	0·2093	73·0	64·8		199	0·1469	0·1480	4·00	—
							197	0·1752	0·1773	3·53	—
78·33	185	0·1040	0·1049	18·1	—		190	0·2025	0·2037	3·60	4·10
	186	0·1335	0·1345	19·9	—						
	175/6	0·1979	0·1985	18·9	17·1	71·48	223/4	0·2099	0·2081	0·254	(0·310)
	184	0·2349	0·2374	16·6	—						
(d) *Variation of temperature.*											
		Temp. 14·8°.						Temp. 35·0°.			
81·14	171	0·1908	0·1928	103	—	81·14	170	0·1914	0·1923	309	—
78·33	188	0·1972	0·1933	7·26	—	78·33	187	0·1974	0·1989	37·0	—
75·47	196	0·2033	0·2029	1·56	—	75·47	195	0·2025	0·2037	8·72	—

Equilibrium Constants.—A further illustration of the validity of the velocity coefficients, k_2 for nitration, and k_1 for denitration lies in comparing the values of the empirical equilibrium product K of equation (5) (determined from *end-point measurements*, as described in Part I, the subscript e denoting equilibrium concentrations)

$$K = [\mathrm{PH^+}]_e/[\mathrm{GH^+}]_e[\mathrm{HNO_3}]_e \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (5)$$

with equilibrium products calculated from initial reaction rates by the relation $K = k_2/k_1$. The comparison is shown in Table 3. Agreement is reasonable in view of the experimental errors involved. The ratios k_2'/k_1' refer to coefficients derived from equation (6).

TABLE 2. *Denitration of nitroguanidine at 25°.*

Medium, % H_2SO_4	Expt. no.	Nitro-guanidine, initial concn., M	Time for 5% denitration, min.	10^4k_1
82·94	235/237/238	0·2084	—	277
79·24	232	0·0500	8·0	68·2
	231	0·1041	8·5	64·5
	230	0·1562	9·7	57·6
	228/229	0·2084	8·7	55·5
	233	0·3047	9·7	48·0
	234	0·4146	12·3	41·5
75·47	216/217	0·1000	50	10·6
	207/213/214	0·2024	57	9·45
	215/218	0·4000	77	6·80
71·48	239/240	0·2082	—	1·80

TABLE 3. *Equilibrium products for* 0·2M-*initial reagent concentrations.*

Medium, % H_2SO_4	82·94	79·24	75·47	71·48
K (end-point)	294	114	44·6	—
k_2/k_1	359	132	38·1	14·1
k_2'/k_1'	332	146	47·1	14·7

The Reversible Kinetic Equation for a Given Medium.—Combination of equations (3) and (4) gives equation (6) as an expression of the reaction rate in the reversible process, in a given medium :

$$-\,\mathrm{d}[\mathrm{HNO_3}]/\mathrm{d}t = k_2[\mathrm{GH^+}][\mathrm{HNO_3}] - k_1[\mathrm{PH^+}] \quad . \; . \; . \; . \; . \; . \quad (6)$$

If a and b are the initial concentrations of guanidinium ion and nitric acid respectively; and if x and z are the concentrations of nitroguanidine at time t and at equilibrium, respectively, integration of (6) gives (7) or (8), according to whether a equals b, or not.

$$k_2t = \frac{2{\cdot}303z}{a^2 - z^2}\log\left\{\frac{z}{a^2}\cdot\frac{a^2 - xz}{z - x}\right\} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (7)$$

$$k_2t = \frac{2{\cdot}303z}{ab - z^2}\log\left\{\frac{z}{ab}\cdot\frac{ab - xz}{z - x}\right\} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (8)$$

Experimentally (as illustrated in Fig. 1, expts. 221/2, 223/4, 225/6), the log terms in (7) and (8) are found to be linear with time for those experiments in Table 1 which were pursued far enough to give z. N-Nitration velocity coefficients, calculated from the linear graphs of (7) and (8), are shown as k_2' in Table 1. As a rule, they do not differ greatly from the values of k_2, calculated, by equation (3), from the measurements of initial rates. Figures for k_2' in parentheses are based on extrapolated values of z.

The Rate-determining Step in N-*Nitration.*—Velocities of N-nitration of the guanidinium ion in 76—82% sulphuric acid are close enough (differing at most by a factor of 2 in a given medium) to the rates of nuclear nitration of the trimethyl-*p*-tolylammonium ion (Williams and Lowen, *J.*, 1950, 3312; Lowen, Murray, and Williams, *ibid.*, p. 3318) in the same media, to raise the suspicion that the measured rate might be the rate of conversion of nitric acid into the actual nitrating agent, as happens in other media (Hughes, Ingold, and Reed, *J.*, 1950, 2400). The possibility is excluded because, in the same medium range, toluene-*p*-sulphonic acid is nitrated much more rapidly than either compound. Thus, 0·085M-toluene-*p*-sulphonic acid was completely mononitrated in less than 1·5 min. in 79% sulphuric acid at 25°, whereas 0·2M-guanidine required 51 min. for 81% nitration (equilibrium) in the same medium. The guanidinium ion is not, therefore, being rapidly attacked by a slowly formed nitrating agent.

The Nitrating Agent in N-*Nitration*.—The velocity coefficient, k_2 of equation (3), for N-nitration of the guanidinium ion falls by a factor of 4×10^3 in the medium range 83—71·5% sulphuric acid [Table 1 (c)]; and therefore decreases far more steeply than the vapour pressure of nitric acid over its solutions in the same media. The argument against supposing the un-ionised nitric acid molecule to be the nitrating agent is the same as for the nuclear nitration of the trimethyl-p-tolylammonium ion (*loc. cit.*). A positive test for nitration by the nitronium ion can also be applied to guanidine, as to the aromatic ion (*loc. cit.*, cf. Westheimer and Kharasch, *J. Amer. Chem. Soc.*, 1946, **68**, 1871).

If the experimental and theoretical rates of N-nitration are given by equations (3) and (9), respectively, and if equation (10) defines an acidity function J_0, governing the ionisation of a carbinol ROH (Lowen, Murray, and Williams, *loc. cit.*; Gold and Hawes, *J.*, 1951, 2102), then, provided that (11) holds, with b independent of medium, and that (12) is valid throughout the medium range, equation (13) follows (Bonner, Bowyer, and Williams, *J.*, 1952, 3274), by analogy with an argument due to Hammett and Paul (*J. Amer. Chem. Soc.*, 1934, **56**, 830).

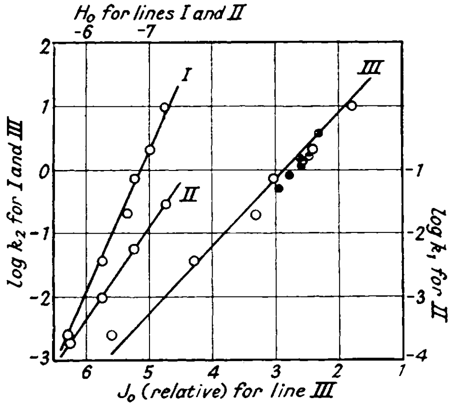


FIG. 3.

⊗ *Varying guanidine concentration.*
◓ *With added* $\mathrm{KHSO_4}$.
● *With added* $\mathrm{(NH_4)_2SO_4}$.

$$-d[\mathrm{HNO_3}]/dt = k_2^\circ[\mathrm{NO_2^+}][\mathrm{GH^+}] \quad . \; . \; . \; . \; . \; . \; . \; . \quad (9)$$

$$J_0 = -\mathrm{p}K_{\mathrm{NO_2\cdot OH}} - \log([\mathrm{NO_2^+}]/[\mathrm{NO_2\cdot OH}]) \quad . \; . \; . \; . \; . \; . \; . \quad (10)$$

$$[\mathrm{NO_2^+}]/[\mathrm{NO_2\cdot OH}] = b\,.\,[\mathrm{R^+}]/[\mathrm{R\cdot OH}] \quad . \; . \; . \; . \; . \; . \; . \; . \quad (11)$$

$$[\mathrm{HNO_3}] = [\mathrm{NO_2^+}] + [\mathrm{NO_2\cdot OH}] \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (12)$$

$$\log k_2 = \log k_2^\circ - \mathrm{p}K_{\mathrm{NO_2\cdot OH}} - J_0 - \log\left\{1 + \frac{[\mathrm{NO_2^+}]}{[\mathrm{NO_2\cdot OH}]}\right\} \quad . \; . \; . \; . \; . \quad (13)$$

In 83—71% sulphuric acid media, $[\mathrm{NO_2\cdot OH}] \gg [\mathrm{NO_2^+}]$ (cf. Bonner and Williams, *Chem. and Ind.*, 1951, 820). Consequently, from (14), the variation of $\log k_2$ with medium

$$\log k_2 = \log k_2^\circ - \mathrm{p}K_{\mathrm{NO_2\cdot OH}} - J_0 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (14)$$

composition should be connected with that of J_0 ($K_{\mathrm{NO_2\cdot OH}}$ having been defined as a thermodynamic equilibrium constant) by a straight line of negative unit gradient, except in so far as k_2° varies with medium.

The acidity function J_0 is given in absolute terms by the alternative definition, $J_0 = H_0 + \log a_{\mathrm{H_2O}}$ (Gold and Hawes, *loc. cit.*); but, when calculated from this equation, J_0 carries the combined errors in the measurements of both H_0 (Hammett's acidity function) and $a_{\mathrm{H_2O}}$. We have therefore used relative values of J_0 derived directly from measurements of the extent of ionisation of carbinol indicators (Murray and Williams, *J.*, 1950, 3322).

Log k_2 is plotted against J_0 (rel.) in Fig. 3 (line III). The points are somewhat scattered, but the slope, calculated by the method of least squares, for the line shown in the diagram, is $-1{\cdot}06$ in accordance with equation (14).* If the $H_2NO_3^+$ ion were the nitrating agent, log k_2 should give a straight line of unit slope when plotted against $-H_0$. Fig. 3 also shows that the graph of log k_2 against H_0 has a slope of $-2{\cdot}2$ (line I).

The graphs in Fig. 3 suffice to show clearly that the hypothesis of *N*-nitration by the NO_2^+ ion is preferable to that of nitration by the $H_2NO_3^+$ ion (cf. Blackall and Hughes, *Nature*, 1952, **170**, 972). Evidently, however, the conformation of the points to the calculated line

$$\log k_2 = -1{\cdot}056 J_0 + 3{\cdot}008 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (15)$$

is not exact. A curve could be drawn through them. The curvature (if real) could be due (*a*) to experimental error, (*b*) to a medium variation of b in equation (11), (*c*) to a medium variation of k_2° in equation (14). Insufficient information is available at present to warrant a decision between these possibilities.

It is also difficult to judge whether appreciable ionisation of nitric acid to nitrate ion impairs the validity of equation (12) in the most aqueous media employed (*e.g.*, in 71·5% sulphuric acid). Raman spectra of nitric acid are not decisive in such solvents (Chédin, *Ann. Chim.*, 1937, **8**, 243); but the ultra-violet absorption maximum of the nitrate ion is not evident in solutions of nitric acid in 70% sulphuric acid (unpublished experiments; cf. Schaefer, *Z. anorg. Chem.*, 1916, **98**, 77). Evidence for hydrated forms of molecular nitric acid in nitric acid–water mixtures has recently been discussed by Chédin (*J. Chim. phys.*, 1952, **49**, 109).

Influence of Initial Guanidine Concentration.—The variation of k_2 with initial guanidine concentration in a given medium, shown in Table 1(b), may be due (*a*) to an influence of changing concentration upon the theoretical velocity coefficient k_2° of equation (9), (*b*) to an influence of the guanidine salt upon the acidity of the medium with a consequent alteration of the degree of ionisation of nitric acid to the nitronium ion, or (*c*) to both.

Influence of Added Salts.—The effect referred to in the preceding paragraph is closely connected with the influence of added inorganic salts upon the rate of *N*-nitration shown by the results in Table 4. The influence of salts may also be considered under the headings (*a*), (*b*), and (*c*) of the preceding section. There is provisional evidence that (*b*) is an important factor.

TABLE 4. *Influence of added salts at 25°.*

Medium, 81·14% H_2SO_4. Initial reagent concentrations, 0·2M.

Expt. no.	Added salt and concn., M.		$100k_2$	Expt. no.	Added salt and concn., M.		$100k_2$
160/161	—	—	209	172	$(NH_4)_2SO_4$	0·285	114
				173	$(NH_4)_2SO_4$	0·599	78·7
168	$KHSO_4$	0·299	163	174	$(NH_4)_2SO_4$	0·861	47·5
169	$KHSO_4$	0·557	154				

Variation of the Extent of Ionisation of Nitric Acid.—It is an empirical fact that additions of salts (including guanidine salts) bring about an apparent change in the extent of ionisation of a triarylcarbinol indicator in media within the range 71·5—83% sulphuric acid as measured colorimetrically (at a single wave-length) with a photoelectric absorptiometer. If the alteration of intensity of light absorption is really due to altered extent of ionisation, then J_0 for the medium—equation (10)—is affected by salt additions; and these will also influence the extent of ionisation of nitric acid to nitronium ion. Unpublished experiments (by Dr. M. A. Murray) give ΔJ_0/mole for potassium hydrogen sulphate, ammonium sulphate, and guanidine carbonate as $-0{\cdot}2$, $-0{\cdot}6$, and $-2{\cdot}0$, respectively, for media in the region of 80% sulphuric acid. The negative sign here indicates lowering of acidity. These figures are approximate and provisional. If they are used to calculate changes of J_0 brought about by the salt concentrations shown in Table 1(b) and in Table 4, and if these concentrations influence nitration speed mainly by their effects upon nitronium-ion concentration, then the corresponding changes of nitration speed should be accommodated by equation (14). Correlation of log k_2 with the calculated values of J_0 is shown in Fig. 3.

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* The less extensive results at other temperatures—Table 1 (d)—give approximately parallel lines. If log k_2 is plotted against Gold and Hawes's values for J_0, the line has a slightly steeper slope than that shown in Fig. 3.

The calculated salt effects appear to be of the right order of magnitude, but the conclusions must be accepted with reserve, pending completion of absorption experiments on carbinol indicators over a range of wave-lengths.

Effect of Temperature upon N-*Nitration.*—Results at different temperatures are shown in Table 1 (d). The Arrhenius equations for 78·3 and 74·5% sulphuric acid are, respectively, $k_2 = 1{\cdot}60 \times 10^7$ exp. $(-13{,}230/\boldsymbol{R}T)$ and $k_2 = 7{\cdot}71 \times 10^7$ exp. $(-13{,}790/\boldsymbol{R}T)$ l. mole^{-1} sec.$^{-1}$. The results for 81·1% sulphuric acid are discordant and require confirmation. They give $k_2 = 8{\cdot}15 \times 10^5$ exp. $(-8{,}940/\boldsymbol{R}T)$.

Nitration and Denitration.—Wright and his colleagues have shown (*Canad. J. Res.*, 1948, **26**, *B*, 104, 114, 257) that easy *N*-nitration to form nitramines is associated with weak basicity of the nitrogen atom at which reaction takes place. Their hypothesis of preliminary formation of an amine–nitric acid complex has been interpreted by Lamberton (*Quart. Reviews*, 1951, **5**, 75) in terms of action by the nitronium ion. The guanidinium ion is a very weak base (unpublished experiments) and its ready *N*-nitration is consistent with these views. The present work supports the hypothesis of nitration by the nitronium ion in 83—71·5% sulphuric acid. A possible scheme for the process (Lamberton, *loc. cit.*) is :

$$\mathrm{NO_2^+ + H_2\overset{+}{N}{:}C(NH_2)_2 \rightleftharpoons H_2\overset{+}{N}{:}C(NH_2){\cdot}\overset{+}{N}H_2{\cdot}NO_2 \rightleftharpoons H_2\overset{+}{N}{:}C(NH_2){\cdot}NH{\cdot}NO_2 + H^+} \; . \quad (16)$$

The coefficient k_1 for the denitration of nitroguanidine falls by a factor of 150 over the range 83—71·5% sulphuric acid (Table 2). If the rate-determining step in the denitration of nitroguanidine were the extrusion of nitronium ion from the transition complex of (16), produced from nitroguanidinium ion by rapid proton uptake, then by Hammett and Paul's argument (*loc. cit.*) log k_1 might be connected by a line of unit negative gradient with the acidity function H_+ governing proton uptake by a positively charged base. No values are available for H_+ in sulphuric acid. The graph of log k_1 against H_0 is shown in Fig. 3 (line II). It has gradient $-1{\cdot}4$. The results are too few to warrant any firm conclusions about the mechanism of denitration.

EXPERIMENTAL

Materials.—" AnalaR " guanidine carbonate was purified by precipitation from a solution in boiling water by addition of alcohol, and dried (P_2O_5) at 50°/10 mm. for 48 hours (Found, for two samples: C, 20·5, 19·8; H, 6·55, 6·2; N, 46·6, 47·0. Calc. for $C_3H_{12}O_3N_6$: C, 20·0; H, 6·7; N, 46·7%).

Inorganic salts were " AnalaR " materials dried before use. All other materials were prepared and purified as described in Part I (*loc. cit.*).

Velocity Measurements.—The guanidine solution was prepared by dissolving guanidine carbonate in sulphuric acid–water medium in a 50-ml. flask in an ice–water bath. After being made up to volume at thermostat temperature, the solution was transferred to a three-necked reaction vessel. To it (with stirring) was added a solution of nitric acid in the same medium. Timing of the reaction was started when the addition of the nitric acid solution (generally requiring 30 sec.) was one-half completed. Corrections were applied for drainage residues left in the standard flasks in which the two reagent solutions had been prepared. Samples for analysis were withdrawn in a 5-ml. pipette fitted with a stopcock. These were poured into 55 ml. of water at recorded times.

For certain very rapid reactions, 5-ml. samples of nitric acid solution were added from B.19 cone caps of 5-ml. capacity to 5-ml. samples of guanidine solution in 10-ml. containers fitted with B.19 sockets, with vigorous shaking. For sampling, the whole contents of each 10-ml. vessel were poured into 10 ml. of water. With this method a sample could be withdrawn within 6 seconds after mixing of the reagents. With a series of the 10-ml. reaction vessels, samples could be timed at 3-second intervals if required (cf. expt. 225/6 in Fig. 1).

The samples extracted from the reaction mixture at recorded times were analysed for nitric acid, after destruction of nitroguanidine, by the method described in Part I (*loc. cit.*).

Duplicate experiments (see Tables), with independent reaction mixtures, were commonly combined to give one reaction curve. Reproducibility may be judged from examples given in Figs. 1 and 2.

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