

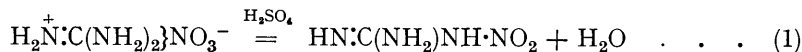
**592.** *The Nitration of Guanidine in Sulphuric Acid. Part I. The Reversible Conversion of Guanidine Nitrate into Nitroguanidine.*

By R. J. J. SIMKINS and GWYN WILLIAMS.

The conversion of guanidine nitrate into nitroguanidine in sulphuric acid-water media is reversible. Equilibrium is approached at a measurable rate, from either side, in 71–83% sulphuric acid, very rapidly in media containing more than 85% sulphuric acid. On the supposition that the effective nitrating agent is the nitronium ion in all the media considered, mass-action considerations predict that conversion into nitroguanidine should be most extensive (for small concentrations) in 90–88% sulphuric acid. This expectation is fulfilled; but the crude mass-action theory does not quantitatively reproduce the actual extent of conversion in its variation with medium. An empirical equilibrium product, *K*, has been measured for 71.5–100% sulphuric acid media at 25°, with 0.2M initial concentration of guanidine nitrate or nitroguanidine. It has a maximum value in 88% sulphuric acid.

A theoretical connection between *K* and the water activity has been derived and verified for 71–86% sulphuric acid media, in which nitric acid is only slightly ionised to the nitronium ion.

WHEN dissolved in concentrated sulphuric acid, guanidine nitrate changes into nitroguanidine [cf. Jousselin (who thought the product was nitrosoguanidine), *Compt. rend.*, 1877, **85**, 548; 1879, **88**, 814, 1086; Pellizzari, *Gazzetta*, 1891, **21**, II, 405; and, especially, Thiele, *Annalen*, 1892, **270**, 1]. This transformation is a common method for preparing nitroguanidine (*e.g.*, Ewan and Young, *J. Soc. Chem. Ind.*, 1921, **40**, 109T; Smith, Sabetta, and Steinbach, *Ind. Eng. Chem.*, 1931, **23**, 1124; Davis, *Org. Synth.*, Coll. Vol. I, 1941, pp. 302, 399), the product being precipitated on dilution of the reaction mixture with water. The overall reaction to form free nitroguanidine is given by equation (1):



That the process is a nitration, and not a dehydration, has been recognised explicitly (*e.g.*, by Davis and Elderfield, *J. Amer. Chem. Soc.*, 1933, **55**, 731).

Barton, Hall, and Wright (*ibid.*, 1951, **73**, 2201) have given reasons for supposing that the nitro-group is attached to the *imino-nitrogen* atom in free nitroguanidine, and not to the amino-nitrogen as represented in equation (1). However, the distinction is immaterial in sulphuric acid solution, because the most probable structures,  $[\text{H}_2\text{N:C}(\text{NH}_2)\text{NH}\cdot\text{NO}_2]^+$  and  $[(\text{H}_2\text{N})_2\text{C:NH}\cdot\text{NO}_2]^+$ , of the ionised forms derived from the two possible formulæ for free nitroguanidine are identical apart from the formal placement of the charge.

Nitroguanidine is a base (though enormously weaker than guanidine; cf. Hall and Sprinkle, *ibid.*, 1932, **54**, 3469) and forms salts, though these are unstable in water (Thiele, *loc. cit.*; Davis, Ashdown, and Couch, *J. Amer. Chem. Soc.*, 1925, **47**, 1063). To precipitate nitroguanidine as free base from sulphuric acid solution, enough water must be added to dilute the sulphuric acid to not more than 20% concentration. If dilution is insufficient, a nitroguanidine sulphate is precipitated. In solution in concentrated sulphuric acid, therefore, nitroguanidine must exist principally as nitroguanidinium ion [equation (5) below]. Guanidine is, of course, a very strong base and will always be present as guanidinium ion (Hall and Sprinkle, *loc. cit.*; Davis and Elderfield, *ibid.*, p. 3470; Angyal and Warburton, *J.*, 1951, 2492).

Although nitroguanidine may be prepared in 90% yield by reaction (1) in sulphuric acid, there are indications that the transformation is reversible in this solvent (as with some other nitramines; cf. Allenby and Wright, *Canad. J. Res.*, 1947, **25**, B, 295; Stuart and Wright, *ibid.*, 1948, **26**, B, 401; Lamberton, *Quart. Reviews*, 1951, **5**, 75): (1) Davis and Abrams (*Proc. Amer. Acad. Arts Sci.*, 1926, **61**, 437) found that nitroguanidine in

concentrated sulphuric acid acted as a nitrating agent towards aniline, phenol, and acetop-*p*-toluidide. The nitrating action has recently been confirmed (personal communication from Dr. A. H. Lamberton). Davis and Abrams did not ascribe the nitrating action to nitric acid formed reversibly from nitroguanidine; for no nitric acid could be distilled from a solution of nitroguanidine in concentrated sulphuric acid; instead, strong heating gave the decomposition products, nitrous oxide, carbon dioxide, and ammonia (Davis, *J. Amer. Chem. Soc.*, 1922, **44**, 868). However, nitric acid *present in small concentration* is not readily recoverable by distillation from concentrated sulphuric acid (Bennett, Brand, and Williams, *J.*, 1946, 870), owing to the formation of nitronium ion. (2) In sulphuric acid solution, nitroguanidine behaves like nitric acid towards analytical reagents. It reacts quantitatively with mercury and sulphuric acid in the nitrometer (Cope and Barab, *J. Amer. Chem. Soc.*, 1916, **38**, 2552); it also responds quantitatively, like nitric acid, to electrometric titration with ferrous sulphate in sulphuric acid (Cottrell, MacInnes, and Patterson, *Analyst*, 1946, **71**, 207). Some results obtained in the present work, by the method of Treadwell and Vontobel (see Experimental section) are given in Table 1.

TABLE 1. *Titration of solutions of nitroguanidine in concentrated sulphuric acid with ferrous sulphate.*

Concn. of nitroguanidine, M .....	0.366	0.415	0.526
Nitrate found, M .....	0.377	0.414	0.524

The reversible interconvertibility of guanidine nitrate and nitroguanidine, in sulphuric acid, is proved explicitly by the following experiments, in which a solution, held at constant temperature, was analysed for nitric acid at known time intervals, by a method which made it possible to determine the nitric acid concentration in a sulphuric acid solution which also contained nitroguanidine. Details are given in the Experimental section.

TABLE 2. *The establishment of equilibrium at 25°.*

Initial concn. of guanidine nitrate = 0.2000M.						Initial concn. of nitroguanidine = 0.2000M.	
Expt. 78		Expt. 82		Expt. 27		Expt. 29	
Medium: 100% H <sub>2</sub> SO <sub>4</sub> .		Medium: 87.8% H <sub>2</sub> SO <sub>4</sub> .		Medium: 97.2% H <sub>2</sub> SO <sub>4</sub> .		Medium: 97.2% H <sub>2</sub> SO <sub>4</sub> .	
Time (mins.)	HNO <sub>3</sub> , M	Time (mins.)	HNO <sub>3</sub> , M	Time (mins.)	HNO <sub>3</sub> , M	Time (mins.)	HNO <sub>3</sub> , M
0	0.2000	0	0.2000	0	0.2000	0	0
8.7	0.1674	9.2	0.0126	2.4	0.1124	1.8	0.1129
12.2	0.1672	13.0	0.0122	5.3	0.1133	5.7	0.1133
17.0	0.1679	16.5	0.0124	9.0	0.1130	9.2	0.1134
20.8	0.1671	21.4	0.0127	12.7	0.1122	13.3	0.1140
27.6	0.1666	27.2	0.0124	19.1	0.1121	19.7	0.1140
34.1	0.1650	36.3	0.0125	32.1	0.1121	36.0	0.1138
67.4	0.1672	52.3	0.0125	55.8	0.1105	59.3	0.1119

*Reversibility of the Reaction.*—When either guanidine nitrate, or an equivalent concentration of nitroguanidine, is dissolved in the sulphuric acid medium, the nitric acid concentration moves rapidly to a constant value which is the same with either starting material. The composition of the equilibrium mixture depends on the medium composition. The experimental proof is given in Fig. 1; and other sample experiments are shown in Table 2.

*Rates of Reaction.*—Expts. 15/16 and 23/24 (see Fig. 1) show that the attainment of equilibrium is very rapid in 85.6% sulphuric acid with 0.027M-reagents. With higher concentrations of guanidine nitrate (*e.g.*, 0.2M), the material takes appreciable time (up to 10 minutes) to dissolve in media weaker than 90% sulphuric acid, though the first measurement made on the homogeneous solution corresponds to the equilibrium composition. It may be assumed, therefore, that the actual chemical reaction is very rapid in media containing more than 85% sulphuric acid. With 0.018M-reagents in 80.7% sulphuric acid (Expts. 18/19), however, the approach to equilibrium takes a measurable time, being incomplete after 1 hour.

*Notation.*—In the following, the symbols G and P stand for the free base molecules of

guanidine and nitroguanidine, respectively. The symbol  $[\text{HNO}_3]$  represents the stoichiometric concentration of nitric acid, as determined by analysis; so that  $[\text{HNO}_3] = [\text{NO}_2^+] + [\text{NO}_2\cdot\text{OH}]$ , if neither  $\text{H}_2\text{NO}_3^+$  nor  $\text{NO}_3^-$  is formed. All concentrations are recorded in moles per litre.

*Mass-action Considerations.*—It is convenient to represent the results of the measurements in terms of an equilibrium product,  $K$ , defined by the equation:

$$K = [\text{PH}^+]_e / [\text{GH}^+]_e [\text{HNO}_3]_e \quad . . . . . (2)$$

$K$  is thus defined by measurable concentrations.  $[\text{GH}^+]$  and  $[\text{PH}^+]$  are, respectively, the concentrations of guanidinium and nitroguanidinium ions. The suffix  $e$  refers to equilibrium concentrations.

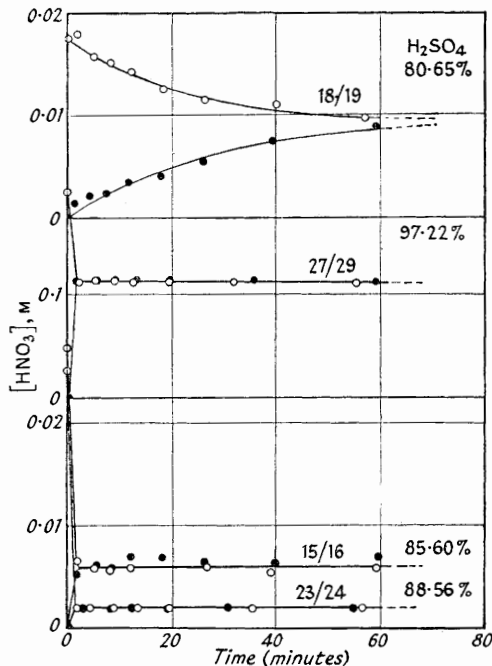
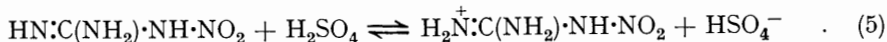
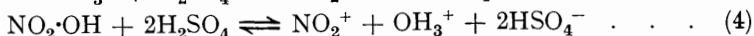
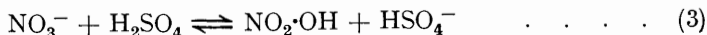


FIG. 1. The guanidine nitrate-nitroguanidine equilibrium.

○, With initial guanidine nitrate.  
●, With initial nitroguanidine.

The overall conversion into neutral nitroguanidine is represented by equation (1). In a medium of concentrated sulphuric acid, however, the following equilibria are set up:



Of these, (3) and (5) probably lie completely, and (6) probably lies substantially, to the right in most of the media considered. The position of (4) depends on the composition of the system. Further equations will be needed if guanidine takes up more than one proton in very concentrated sulphuric acid (see below), and if nitric acid forms any appreciable concentration of nitrate ion in the most aqueous media.

By combining these equations with (1), the nitroguanidine equilibrium may be written:



Equation (7) is based on the assumption that the nitronium ion is the sole nitrating agent. This will be true in media containing 95% of sulphuric acid, or more, in which

equilibrium (4) lies completely to the right (for relatively small concentrations of nitric acid). Whether  $\text{NO}_2^+$  is the sole nitrating agent in more aqueous media, or whether the  $\text{H}_2\text{NO}_3^+$  ion (if present) or the  $\text{NO}_2\cdot\text{OH}$  molecule can also nitrate the guanidinium ion, are matters for investigation. The nitronium ion is formed in sufficient concentration in 75–82% sulphuric acid to be effective in aromatic nitration (Lowen, Murray, and Williams, *J.*, 1950, 3318). Velocity measurements with guanidine nitrate, in 71.5–83% sulphuric acid, furnish evidence that the nitronium ion nitrates guanidine in the same media (unpublished experiments).

From equation (7) an equilibrium constant,  $K_0^\circ$ , may be defined by equation (8) :

$$K_0^\circ = \frac{[\text{PH}^+]_e[\text{H}_2\text{SO}_4]_e}{[\text{GH}^+]_e[\text{NO}_2^+]_e[\text{HSO}_4^-]_e} \cdot \frac{f_{\text{PH}^+}}{f_{\text{GH}^+}} \cdot \frac{f_{\text{H}_2\text{SO}_4}}{f_{\text{NO}_2^+} f_{\text{HSO}_4^-}} \dots \dots \dots (8)$$

If the term in activity coefficients is neglected for the time being, then from (2) and (8)

$$K = K_0 r Q \dots \dots \dots (9)$$

in which  $K_0$  is the "concentration" equilibrium constant for (7), and

$$r = [\text{HSO}_4^-]/[\text{H}_2\text{SO}_4]; Q = [\text{NO}_2^+]/[\text{HNO}_3] \dots \dots \dots (10)$$

Equation (9) can be made to show how the empirical equilibrium product,  $K$ , may be expected to vary with medium composition. For *small* reagent concentrations,  $r \sim r_m$ , in which  $r_m$  is the ratio  $[\text{HSO}_4^-]/[\text{H}_2\text{SO}_4]$  for the sulphuric acid–water medium. In equilibrium (6),  $r_m$  is not known with certainty over any extensive medium range; but Brand has shown (*J.*, 1950, 997) that the equation ( $H_0$  being Hammett's acidity function)

$$\log r_m = H_0 + 8.35 \dots \dots \dots (11)$$

is valid for 87–99.8% sulphuric acid when  $r_m$  is calculated on the supposition that water reacts quantitatively in (6), to form oxonium and bisulphate ions. If equation (11) can be supposed to define  $r_m$  in still more aqueous media [in which (6) certainly does not lie quantitatively to the right], then the calculated  $r_m$  values may be combined with estimates of  $Q$  derived from the combination of carbinol indicator and aromatic nitration measurements (Bonner and Williams, *Chem. and Ind.*, 1951, 820), to give the products  $r_m Q$  for insertion in (9). Relative values of  $r_m Q$  are shown in Table 3.

TABLE 3. Estimate of medium effect on  $K$ .

Medium, $\text{H}_2\text{SO}_4$ , %	99	95	90	89	88	87.5	87	85	82
$r_m Q$ (rel.)	0.076	0.52	1.2	1.2	1.1	1.0	0.78	0.36	0.095
$K$ (obs. rel.)	0.0017	0.022	0.54	0.83	0.98	1.0	0.92	0.53	0.23

*Influence of Medium Composition: Experimental Results.*—Results for the equilibrium product,  $K$ , in different media, are recorded in Tables 4 and 5. All these results were determined from the equilibrium compositions derived from 0.2M-starting materials. With this reagent concentration it is not very accurate to set  $r \sim r_m$  in equation (9). Nevertheless, relative values of  $K$  are put in Table 3 for comparison with the calculated  $r_m Q$ . Quantitatively, equation (9) does not reproduce the decrease of  $K$  from the maximum with any accuracy, particularly in media more acid than the optimum, although it predicts a maximum value for  $K$  in about the right medium.  $K_0$  in (9) is not independent of medium composition.

The results in Table 5 are for media in which the approach to equilibrium is slow enough to be followed from either side. Starting materials for nitration were mixed solutions of guanidine carbonate and nitric acid in the sulphuric acid medium. The values of  $K$  in Table 5, like those in Table 4, are calculated from equilibrium end-point measurements.

*Equilibrium Products from Initial-rate Measurements.*—In the more aqueous media (Table 5) it is also possible to calculate  $K$  as the quotient,  $k_2/k_1$ , of velocity coefficients for initial rates of nitration of the guanidinium ion and of denitration of nitroguanidine. Equilibrium products so derived are shown as blackened circles in Fig. 2. They are in satisfactory agreement with the equilibrium products determined from end-point measurements.

TABLE 4. Influence of medium composition (rapid reactions) at 25°. Initial concentration of guanidine nitrate, 0.2000M.

Expt. no.	Medium: H <sub>2</sub> SO <sub>4</sub> , %	At equilibrium			K	K (mean)
		HNO <sub>3</sub> , M	Nitro-guanidine, M	Conversion into nitroguanidine, %		
76	100	0.1668	0.0332	16.6	1.19	
77	—	0.1682	0.0318	15.9	1.12	1.17
78	—	0.1669	0.0331	16.6	1.19	
42	98.95	0.1536	0.0464	23.2	1.97	
43	—	0.1551	0.0449	22.5	1.87	1.92
134	98.87	0.1464	0.0536	26.8	—	2.50
110	98.64	0.1527	0.0473	23.7	—	2.03
154	98.40	0.1436	0.0564	28.2	—	2.74
27	97.22	0.1122	0.0879	43.9	6.98	
28	—	0.1116	0.0886	44.2	7.12	7.08
32	—	0.1114	0.0886	44.3	7.15	
117	97.11	0.1195	0.0805	40.2	—	5.64
49	95.74	0.0888	0.1112	55.6	14.1	14.2
51	—	0.0883	0.1117	55.9	14.3	
58	93.95	0.0534	0.1466	73.3	51.4	51.2
59	—	0.0536	0.1464	73.2	51.0	
149	93.85	0.0506	0.1494	74.7	—	58.3
139	91.60	0.0261	0.1739	87.0	—	255
64	90.95	0.0216	0.1784	89.2	383	399
65	—	0.0208	0.1792	89.6	414	
70	88.61	0.0135	0.1865	93.3	—	1024
79	87.84	0.0131	0.1869	93.5	1088	
80	—	0.0134	0.1866	93.3	1044	
81	—	0.0127	0.1873	93.7	1166	1121
82	—	0.0125	0.1875	93.8	1205	
83	—	0.0130	0.1870	93.5	1111	
71	87.16	0.0130	0.1870	93.5	—	1113
73	86.70	0.0142	0.1858	92.9	—	916
102	85.03	0.0171	0.1829	91.5	—	628
74	84.90	0.0180	0.1820	91.0	560	543
75	—	0.0186	0.1814	90.1	526	
144	83.79	0.0202	0.1798	89.9	—	441
94	83.09	0.0215	0.1785	89.3	385	385
95	—	0.0216	0.1784	89.2	384	
100	81.84	0.0270	0.1730	86.5	237	235
101	—	0.0273	0.1727	86.4	233	

TABLE 5. Influence of medium composition (slow reactions) at 25°.

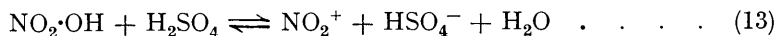
Expt. no.	Medium, H <sub>2</sub> SO <sub>4</sub> , %	Concn. of starting materials			At equilibrium		K
		GH <sup>+</sup> , M	HNO <sub>3</sub> , M	PH <sup>+</sup> , M	HNO <sub>3</sub> , M	% of theor. as PH <sup>+</sup>	
235/7/8	82.94	—	—	0.2084	0.0240	86.8	294
160/1	81.14	0.1907	0.1930	—	0.0288	86.0	212
221/2	79.24	0.2070	0.2093	—	0.0413	80.1	106
228/9	79.24	—	—	0.2084	0.0370	82.9	122
207/13/14	75.47	—	—	0.2024	0.0570	72.0	44.6

*Influence of Medium: Quantitative Treatment.*—From equations (2) and (8),

$$\log K = -pK_0^\circ + \log \frac{[\text{NO}_2^+]}{[\text{NO}_2^+] + [\text{NO}_2 \cdot \text{OH}]} + \log \frac{[\text{HSO}_4^-]}{[\text{H}_2\text{SO}_4]} - \log \left\{ \frac{f_{\text{PH}^+}}{f_{\text{GH}^+}} \cdot \frac{1}{f_{\text{NO}_2^+}} \cdot \frac{f_{\text{H}_2\text{SO}_4}}{f_{\text{HSO}_4^-}} \right\} \quad (12)$$

in which all concentrations refer to the equilibrium state.

If (4) is split formally into (6) and (13)



then for (13) (which may have physical significance in the less acid media),

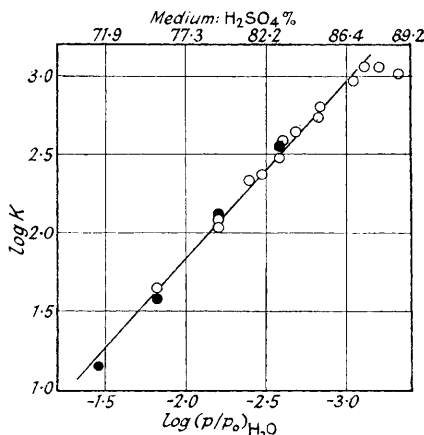
$$\log K_{13}^\circ = \log \frac{[\text{NO}_2^+]}{[\text{NO}_2 \cdot \text{OH}]} + \log \frac{[\text{HSO}_4^-]}{[\text{H}_2\text{SO}_4]} + \log a_{\text{H}_2\text{O}} + \log \left\{ \frac{f_{\text{NO}_2^+}}{f_{\text{NO}_2 \cdot \text{OH}}} \cdot \frac{f_{\text{HSO}_4^-}}{f_{\text{H}_2\text{SO}_4}} \right\} \quad (14)$$

Media on the aqueous side of the optimum may be treated by putting  $[\text{NO}_2 \cdot \text{OH}] \gg [\text{NO}_2^+]$  in (12). Then, from (12) and (14),

$$\log K = -pK_0^\circ - pK_{13}^\circ - \log a_{\text{H}_2\text{O}} - \log \left\{ \frac{f_{\text{PH}^+}}{f_{\text{GH}^+}} \cdot \frac{1}{f_{\text{NO}_2 \cdot \text{OH}}} \right\} \quad (15)$$

The variation of the  $f$ -term in (15) with medium may be expected to depend mainly on the variation of  $f_{\text{NO}_2 \cdot \text{OH}}$ ; and this may be relatively slight in the range 85–70% sulphuric

FIG. 2. Equilibrium product and water activity in sulphuric acid media.



acid, where the system is always loaded with electrolyte. If  $f_{\text{NO}_2 \cdot \text{OH}}$  does not vary greatly, then  $\log K$  should be connected with  $\log a_{\text{H}_2\text{O}}$  by a straight line of slope  $-1$ . Essentially the same result may be obtained from equation (12) and an equation of type (11), together with the equation,  $J_0 = -pK_{\text{NO}_2 \cdot \text{OH}} - \log\{[\text{NO}_2^+]/[\text{NO}_2 \cdot \text{OH}]\}$ , defining an acidity function  $J_0$  for carbinol ionisation (Lowen, Murray, and Williams, *loc. cit.*), and the alternative (and equivalent) definition,  $J_0 = H_0 + \log a_{\text{H}_2\text{O}}$ , of Gold and Hawes (*J.*, 1951, 2102).

In Fig. 2,  $\log K$  is plotted against  $\log (p/p_0)$ , the vapour-pressure ratio for water over sulphuric acid–water mixtures, as tabulated by Gold and Hawes (*loc. cit.*)\*. That the points can be connected by a straight line is no matter for surprise; but the gradient of  $-1.1$  is significant and is consistent with equation (15), implying that equation (12) is a plausible description of the variation of  $K$  with medium composition when nitric acid is only slightly ionised to the nitronium ion. The relation in Fig. 2 appears to hold up to a medium strength of 86–87% sulphuric acid, in which the ratio  $[\text{NO}_2^+]:[\text{HNO}_3]$  is probably 0.08–0.16 (Bonner and Williams, *loc. cit.*).

For large ionisations of nitric acid, equation (15) is naturally invalid; and Table 3 has already shown that a simple mass-action theory, based on equations (9–11), is incapable of accounting for the large fall in  $K$  in the medium range 88–100% sulphuric acid. According to Hantzsch (*Ber.*, 1930, **63**, 1782), guanidine acts as a triacid base in nearly anhydrous sulphuric acid. The formation of ions  $\text{H}_2\text{N}:\text{C}(\text{NH}_2)\cdot\text{NH}_3^{2+}$  and  $\text{H}_2\text{N}:\text{C}(\text{NH}_3)_2^{3+}$ , in the most concentrated sulphuric acid media, would diminish  $K$ . Even if correct, this is not likely to be the only factor which invalidates the simple mass-action theory in the most acid media.

\* In Fig. 2, no allowance can be made for the influence of the reagents (total concn. 0.2M) on  $\log a_{\text{H}_2\text{O}}$ . The change in their influence, over the medium range in question, is possibly not great.

## EXPERIMENTAL

*Materials.*—Pure guanidine nitrate and nitroguanidine were given to us through the kind assistance of Dr. T. M. Walters.

The guanidine nitrate was recrystallised twice from water or methyl or ethyl alcohol and dried at 80—110° for 20 hours before use. It had m. p. 215° (uncorr.) (Found, for two samples: C, 10.35, 10.4; H, 4.9, 5.0; N, 45.2, 45.1%. Calc. for  $\text{CH}_6\text{O}_3\text{N}_4$ : C, 9.8; H, 4.95; N, 45.9%). Its nitrate content was tested by the analytical method described below (Calc. for an aqueous solution:  $[\text{NO}_3^-] = 0.0870\text{M}$ . Found: 0.0875, 0.0875, 0.0875, 0.0877, 0.0879, 0.0873, 0.0875M; mean, 0.0876M).

The nitroguanidine [m. p. 224—226° (decomp.)] was dried over phosphoric oxide for 17 hours at 65°/10 mm. Recrystallisation from boiling water or other solvents was deleterious. Freedom of the material from inorganic impurity is shown by its quantitative titration with ferrous sulphate in concentrated sulphuric acid (see Table 1).

Sulphuric acid media were standardised against *N*-sodium hydroxide, referred, through *N*-hydrochloric acid, to potassium iodate as ultimate standard. Each medium was analysed by six titrations. A typical example gave 82.77, 82.69, 82.85, 82.89, 82.76, 82.93, mean 82.81% of sulphuric acid. 100% Sulphuric acid was prepared by adjustment to maximum freezing point.

*Analytical Solutions.*—For the nitrate determinations, a saturated stock solution of "AnalaR" ferrous ammonium sulphate in *N*-sulphuric acid was diluted with *N*-sulphuric acid to the appropriate concentration (0.05—0.5*N*), and standardised against potassium dichromate. Identical values were obtained with the "dead stop" end-point (see below) and with "ferroin" indicator. The dichromate solution was used as a direct standard and cross-checked against standard iodate.

*Determination of Equilibrium Composition.*—A known weight of guanidine nitrate (or nitroguanidine) was introduced from a weighing bottle (fitted with B.24 cone, and socket cap) by inverting this in the B.24 socket neck of a flask of 100-c.c. capacity, containing a known weight of sulphuric acid medium at thermostat temperature. With about 0.2*M*-reagent, solution took about 15 seconds in 100% and about 9 minutes in 81.9% sulphuric acid. The homogeneous solution was transferred to a three-necked reaction vessel, carrying a stirrer and a thermometer well, in the thermostat. Samples (5 ml.) were extracted at intervals, through the third neck (closed by a ground cap), to be analysed for nitric acid, by means of a pipette (pre-heated to 25°) fitted with a tap above the mark. Since it was the final equilibrium composition which had to be measured, and not the speed of attainment of equilibrium, it was essential only to ensure that the *final* solution was accurately at 25° (more exactly, 24.91°).

Nitroguanidine could not be dissolved, in the above manner, in sulphuric acid stronger than 98%, because the heat of solution caused decomposition.

Volumetric glassware was calibrated. Pipettes for sampling were calibrated to deliver sulphuric acid solutions at the appropriate temperature.

*Analytical Methods.*—The very convenient electrometric titration with ferrous sulphate in concentrated sulphuric acid (Treadwell and Vontobel, *Helv. Chim. Acta*, 1937, **20**, 573) cannot be used for nitric acid in presence of nitroguanidine (Table 1). A modification of the method of Kolthoff, Sandell, and Moskovitz (*J. Amer. Chem. Soc.*, 1933, **55**, 1454; cf. Williams and Lowen, *J.*, 1950, 3312) can be employed instead.

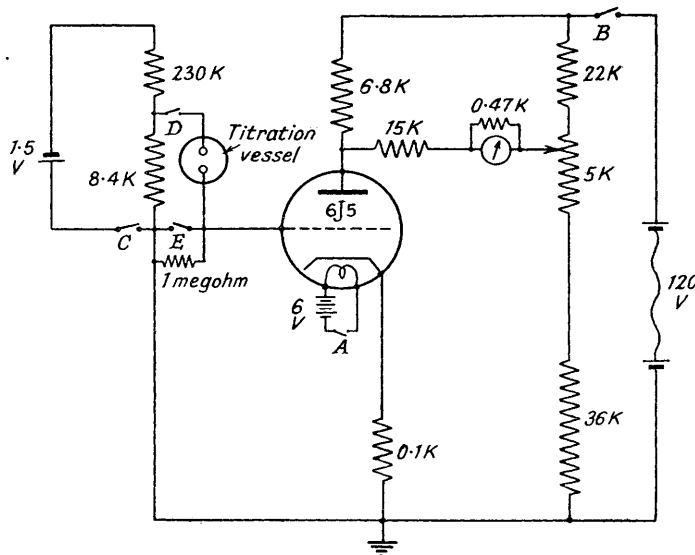
In this method, nitrate is reduced to nitric oxide, in the absence of air, by boiling it with excess of standard ferrous sulphate, in hydrochloric acid medium, with ammonium molybdate as catalyst. The reaction is completed by expelling nitric oxide; and the residual ferrous sulphate is titrated with potassium dichromate. For the nitroguanidine reaction, this method has the advantage that the sample may be drowned in water, to freeze the equilibrium composition. However, nitroguanidine is partly decomposed, during this process of analysis, forming nitrate, and causing a 5% error.

It is therefore necessary to destroy the nitroguanidine present, before analysing for nitrate. This can be done by the action of hot alkali, which decomposes nitroguanidine into nitrous oxide, ammonia, and carbon dioxide (Franchimont, *Rec. Trav. chim.*, 1891, **10**, 233; Thiele, *loc. cit.*). Excess of alkali advantageously stabilises nitric acid as metallic nitrate, while the nitroguanidine is being destroyed. The following standardised procedure has given successful results.

*Procedure.* The 5-ml. sample of sulphuric acid medium, containing nitric acid and nitroguanidine, is run into 55 ml. of water, and the walls of the vessel are washed with a further

15 ml. of water. After 2 minutes, 30 ml. of 50% (w/v) sodium hydroxide solution are added. (The solution may be safely preserved for analysis in this condition.) The solution is boiled (total heating time, 12 minutes), to destroy nitroguanidine. It is then cooled in ice-water, in an atmosphere of carbon dioxide. After 2.5 minutes' cooling, the sample is acidified with 70 ml. of 36% hydrochloric acid. An inert atmosphere in the flask is conserved by carbon dioxide evolved from sodium carbonate formed during the previous operation. To the acid solution, 15 ml. of standard ferrous ammonium sulphate solution (0.05—0.5N) are added from an automatic burette. The flask is fitted with a rubber cork carrying a tap-funnel and an exit tube. When the (yellow) solution starts to boil (3—4 minutes), a 1% solution of ammonium molybdate (about 6 ml.) is run in. The colour of the solution changes to green and, after further boiling, to orange, which signifies that the reaction between ferrous ion and nitrate is complete. Boiling is continued until a total time of 24 minutes has passed. The solution is cooled in ice-water (inert atmosphere) for 4 minutes to about 10°; and then transferred to a beaker. The volume is made up to 140 ml. with water (to dissolve salts precipitated during the previous concentration), and the excess of ferrous ion in the solution is titrated with standard potassium

FIG. 3.



dichromate delivered from a micro-burette. The end-point is detected by the electrometric "dead-stop" method (Fouk and Bowden, *J. Amer. Chem. Soc.*, 1926, **48**, 2045), which has been made more sensitive by a D.C. amplifier. A potential difference of the order 15 mv. is applied across two platinum-wire electrodes in the acid ferrous salt solution being titrated. During titration the potential difference across the electrodes is applied as a potential to the grid of a triode valve. Changes in the anode potential are recorded on a galvanometer, which registers a "kick" of increasing magnitude (up to 80 scale-divisions) as the end-point is approached. As soon as the end-point is passed, the galvanometer needle swings in the opposite direction. The circuit is shown in Fig. 3.

During titration the solution is mechanically stirred and a carbon dioxide atmosphere is maintained above the liquid.

Solutions of widely varying concentrations may be analysed by this method, but at low concentrations (0.02M) a "blank correction" (equivalent to 0.0015M-nitrate) becomes an appreciable fraction of the ferrous ion consumed. The correction was applied to all titrations to allow for "blank" loss of ferrous ion which occurred during the (standardised) process of analysis and could not be eliminated. The "blank" correction amounts to some 10% of the equilibrium nitrate concentration when  $K$  is near its maximum (Table 4). For other conditions it is much less significant.

When a series of samples is to be analysed, the operations may be conveniently staggered by a routine process. Eight samples can be analysed in 2 hours.



*Tests of Method.*—(a) *On solutions in sulphuric acid.* Solutions containing potassium nitrate, with or without nitroguanidine, in concentrated sulphuric acid, gave the following results :

Nitroguanidine, m .....	0	0	0	0.5	0	0.5	0	0.5
Nitrate found, m .....	0.1349	0.1328	0.1321 *	0.1344	0.1327	0.1372 *	0.1341	0.1341
	Mean, nitrate found: 0.1340m. Calc., 0.1339m.							

These were early results, obtained before certain refinements of method had been introduced. The mean error of the eight estimations is 0.87%, or, by disregard of the values marked with an asterisk, 0.52%.

(b) *On aqueous potassium nitrate solutions.* These contained no nitroguanidine, and the alkali treatment was omitted. Nitrate found: 0.0995, 0.0993, 0.0977, 0.0999, 0.0991; mean 0.0991m. Calc.: 0.0990m.

(c) *On aqueous solutions of guanidine nitrate.* (i) Figures obtained without alkali treatment have already been given in the discussion of the purity of the guanidine nitrate.

(ii) The following results were obtained by subjecting aqueous solutions of guanidine nitrate (with or without nitroguanidine) to the whole analytical procedure, including alkali treatment :

Nitroguanidine, m .....	0	0.4	0	0.4	0	0	0.4
Nitrate found, m .....	0.0784	0.0786	0.0788	0.0795	0.0791	0.0789	0.0781
	Mean, nitrate found: 0.0788m. Calc.: 0.0793m.						

These final results confirm (a) that the nitroguanidine is effectively destroyed and does not interfere with the nitrate estimation, and (b) that no nitrate is artificially created by decomposition of the guanidinium ion during the analytical process.

The accuracy of the method seems to be within  $\pm 0.8\%$ .

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