13. *The Denitration of* N-*Methyl*-N′-*nitroguanidine.*

By Muriel L. Hardy-Klein.

The denitration of *N*-methyl-*N′*-nitroguanidine in sulphuric acid is examined. In the range 71—82% sulphuric acid the reaction is of first order with respect to methylnitroguanidine for a fixed initial concentration of methylnitroguanidine in a particular medium. Correlation of rate constants with acidity suggests that the reaction is bimolecular, of the type :

$$\mathrm{MePH^+ + HA \longrightarrow products}$$

where $\mathrm{MePH^+}$ represents the methylnitroguanidine cation and HA the acid species H_2SO_4 and H_3O^+.

The equilibrium between methylnitroguanidine and methylguanidine in sulphuric acid is similar to that for the unmethylated compounds [1] and the nitronium ion is confirmed as the active entity in the nitration of methylguanidine.[2]

Nitramides and nitroguanidines are denitrated when dissolved in concentrated sulphuric acid,[1-4] and denitration proceeds till equilibrium is reached between the nitro-compound

[1] Simkins and Williams, *J.*, 1952, 3086.

[2] *Idem.*, *J.*, 1953, 1386.

[3] Holstead and Lamberton, *J.*, 1952, 1886.

[4] Holstead, Lamberton, and Wyatt, *J.*, 1953, 3341.

and the amide or guanidine. In this paper the denitration of methylnitroguanidine has been investigated. The reverse process, namely the nitration of amides or guanidines, has been examined by Holstead, Lamberton, and Wyatt[4] and by Simkins and Williams;[1,2] the latter showed that for guanidine the nitronium ion is the active nitrating entity in 71—83% sulphuric acid.

Methylnitroguanidine was chosen because it was thought that it would be denitrated more extensively than nitroguanidine. This would have been an advantage as Simkins and Williams[2] were unable to obtain accurate velocity constants for the denitration of nitroguanidine since the extent of denitration of this compound was always small. Although in fact methylnitroguanidine is denitrated only to the same extent as nitroguanidine, Simkins and Williams's difficulties were overcome (*a*) by use of a spectrometric analytical technique which measured the concentration of methylnitroguanidine and not the concentration of nitric acid, as Simkins and Williams had done, (*b*) by always following the reaction to completion so that the velocity constants could be obtained accurately from a reversible kinetic equation, and (*c*) by following the denitration for solutions containing the reagent at a concentration of one-tenth that used by Simkins and Williams so that the degree of denitration at equilibrium was automatically increased.

In 71—82% sulphuric acid the denitration of methylnitroguanidine is sufficiently slow for velocity constants to be obtained. In solutions containing more than 82% sulphuric acid the denitration is rapid, and for such media the equilibrium positions for an initial concentration of 0·02M-methylnitroguanidine have been found.

Reversibility of the Reaction.—As was expected by analogy with nitroguanidine, when methylnitroguanidine, or an equivalent concentration of methylguanidine nitrate, is dissolved in sulphuric acid, the concentration of methylnitroguanidine moves to a constant value which is the same for either starting material (cf. Table 1). The composition at equilibrium and also the rate at which equilibrium is attained depend on the medium strength.

TABLE 1. *The reversible conversion of methylnitroguanidine* (MeP) *into methylguanidine nitrate* ($MeGNO_3$) *at* 25°.

Expt. No.	% H_2SO_4	Initial [MeP] [a]	Initial [$MeGNO_3$] [a]	[MeP] at at equil.[a]	k_1 [b]	k_2 [c]	$K' = k_2/k_1$ [d]	K [d]
102	80·78	0·03998	—	0·02936	0·0501	—	229	260·2
103	,,	,,	—	0·02945	0·0496	—		265·2
104	,,	—	0·03998 *	0·02922	—	11·26		252·3
105	,,	—	,,	0·02924	—	11·49		253·5
108	77·58	0·02000	—	0·010225	0·01043	—	105·1	107·0
109	,,	,,	—	0·010245	0·01048	—		107·6
116	,,	—	0·02000	0·01022	—	1·091		106·9
117	,,	—	,,	0·01020	—	1·106		106·2

* Added as methylguanidine sulphate to 0·3998M-nitric acid.
[a] mole $l.^{-1}$ [b] $min.^{-1}$. [c] l. $mole^{-1}$ $min.^{-1}$. [d] l. $mole^{-1}$.

A Side Reaction to Denitration.—If for a solution of methylnitroguanidine in sulphuric acid the relation between methylnitroguanidine concentration and time is examined, it is found that, although the methylnitroguanidine concentration falls to a value initially constant within the experimental error, after a further lapse of time the concentration is noticeably lower than this value. The data of Table 2 illustrate this fall in concentration, which is due to an irreversible decomposition of methylnitroguanidine similar to that found by Holstead *et al.*[4,5] for solutions of nitrourea, nitrourethane, and for nitroguanidine in sulphuric acid. It is fortunately sufficiently slow to be neglected when rates of denitration are computed since in such reactions a steady equilibrium value is always maintained before decomposition becomes evident (Table 2, expt. 83).

Denitration of Methylnitroguanidine.—For solutions of methylnitroguanidine in 71·7—81·3% sulphuric acid it was possible to measure the rate of approach to equilibrium by

---

[5] Holstead and Lamberton, *J.*, 1954, 2391.

following the change in methylnitroguanidine concentration. To obtain denitration velocity coefficients from such data it was necessary to use an expression in which the reverse nitration was allowed for, since the equilibrium concentrations corresponded to 20—73% conversion of the methylnitroguanidine into methylguanidine. If denitration for a given medium is represented by the rate equation

TABLE 2. *Decomposition of methylnitroguanidine at* 25°.

(Initial concentration of methylnitroguanidine = 0·02000M.)

Expt. 69		Expt. 73		Expt. 83			
94·64% H_2SO_4		93·28% H_2SO_4		79·36% H_2SO_4		79·36% H_2SO_4	
Time (min.)	[MeP] (mole $l.^{-1}$)	Time (min.)	[MeP] (mole $l.^{-1}$)	Time (min.)	[MeP] (mole $l.^{-1}$)	Time (min.)	[MeP] (mole $l.^{-1}$)
11	0·006485	10	0·009656	4	0·01796	51	0·01195
16	0·006468	14·5	0·009625	6	0·01724	100	0·01183
21	0·006503	19·5	0·009588	9	0·01615	150	0·01186
27	0·006431	23	0·009570	12	0·01520	200	0·01179
120	0·006089	193	0·008853	16	0·01421	1100	0·01169
		285	0·008360	30	0·01254		

$$-\mathrm{d}[\mathrm{MePH}^+]/\mathrm{d}t = k_1[\mathrm{MePH}^+] \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and the nitration by

$$\mathrm{d}[\mathrm{MePH}^+]/\mathrm{d}t = k_2[\mathrm{MeGH}^+][\mathrm{HNO}_3] \quad . \quad . \quad . \quad . \quad (2)$$

(cf. Simkins and Williams [2]) where [MePH$^+$] and [MeGH$^+$] are, respectively, the concentrations of methylnitroguanidine and methylguanidine cations, and [HNO$_3$] represents the stoicheiometric concentration of nitric acid, *i.e.*,

$$[\mathrm{HNO}_3] = [\mathrm{NO}_3^-] + [\mathrm{NO}_2\cdot\mathrm{OH}] + [\mathrm{H}_2\mathrm{NO}_3^+] + [\mathrm{NO}_2^+],$$

then the expression for the reaction rate in the reversible process is

$$-\mathrm{d}[\mathrm{MePH}^+]/\mathrm{d}t = k_1[\mathrm{MePH}^+] - k_2[\mathrm{MeGH}^+][\mathrm{HNO}_3] \quad . \quad . \quad . \quad (3)$$

Integration of (3) gives an expression for the rate constant k_1, namely,

$$k_1 = \frac{2\cdot303z}{t(2a - z)}\log\left\{\frac{az + x(a - z)}{a(z - x)}\right\} \quad . \quad . \quad . \quad . \quad (4)$$

where a is the initial concentration of methylnitroguanidine, x the concentration of methylguanidine at time t, and $z = x$ at equilibrium when $\mathrm{d}x/\mathrm{d}t = 0$. Hence, if the denitration of methylnitroguanidine is of first order with respect to methylnitroguanidine, a plot of the log term in eqn. (4) against time should be linear, passing through the origin, and from it k_1 may be calculated. For all the denitrations followed (as illustrated in Fig. 1) such plots were accurately straight lines to about 85% of the equilibrium value. It is thus established that, for a fixed initial concentration of methylnitroguanidine in a particular medium, the rate of denitration is proportional to the first power of the concentration of methylnitroguanidine.

The Methylnitroguanidine Cation.—In all the solutions of methylnitroguanidine in sulphuric acid investigated kinetically methylnitroguanidine was at least monoprotonated. This follows from the value of pK_a for methylnitroguanidine. Ultraviolet spectra of methylnitroguanidine were obtained for a series of solutions in 0—70% sulphuric acid (essentially similar to those for nitroguanidine in hydrochloric acid given be Hall, De Vries, and St. Clair Gantz [6]) and from the relation $H_0 = \mathrm{p}K_a + \log_{10}\{[\mathrm{Base}]/[\mathrm{Ion}]\}$(Brand,

---

[6] Hall, De Vries, and St. Clair Gantz, *J. Amer. Chem. Soc.*, 1955, **77**, 6507.

Horning, and Thornley [7]) pK_a was calculated (Table 3). The mean value is −0·89 and this corresponds to complete protonation of methylnitroguanidine in dilute solution in acids above 70% sulphuric.

TABLE 3. pK_a *for methylnitroguanidine at* 25°, *calculated for* λ = 2600 Å.

% H_2SO_4	9·92	15·93	21·99	29·78
H_0	−0·15	−0·59	−1·01	−1·52
ε_{2600} Å	10,420	8450	6040	3410
pK_a	−0·83	−0·87	−0·91	−0·94

ε_{2500} Å, for MePH$^+$ 1045, for MeP 12,360.

The presence of any considerable concentration of the diprotonated form of methylnitroguanidine in sulphuric acid above 70% is unlikely. It follows from the order of magnitude of pK_a^{I} for guanidine,[8] pK_a^{I} ∼−11, that guanidine does not form a doubly charged cation to any considerable extent in acids below 99% sulphuric. By analogy the weakly basic nitroguanidine is not expected to become doubly charged.

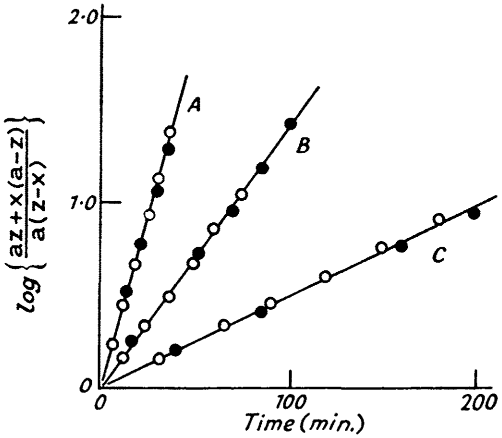


FIG. 1.
Medium: 77·85% H_2SO_4.
Temp.: *A*, 34·98°; *B*, 24·92°; *C*, 14·96°.

TABLE 4. *Influence of medium composition at* 25°.

(Initial concentration of methylnitroguanidine, 0·02000M.)

Expt. No.	% H_2SO_4	k_1 (min.$^{-1}$)	k_1, mean (min.$^{-1}$)	K (l. mole^{-1})	k_2 (l. mole^{-1} min.$^{-1}$)
49	81·30	0·0509	0·0514	291	14·97
71	,,	0·0520	—	—	—
83	79·36	0·0254	0·0252	178	4·49
84	,,	0·0251	—	—	—
78	78·47	0·0173	0·0172	138	2·37
79	,,	0·0175	—	—	—
82	,,	0·0169	—	—	—
108	77·58	0·01043	0·01045	107·3	1·118
109	,,	0·01048	—	—	—
80	75·34	0·00370	0·00371	62	0·2300
81	,,	0·00373	—	—	—
124	71·70	0·000719	0·000709	25·7	0·01821
125	,,	0·000699	—	—	—

The Variation of Velocity Constants with Medium Composition.—Values of k_1, for 0·02M-solutions at 25°, derived by using eqn. (4), are tabulated in Table 4, and they show a sharp increase with increasing acid concentration.

---

[7] Brand, Horning, and Thornley, *J.*, 1952, 1374.
[8] Williams and Hardy, *J.*, 1953, 2560.

The simplest interpretation of this result would be in terms of a unimolecular mechanism which can be written:

$$\mathrm{MePH^+ + H^+ \rightleftharpoons MePH_2^{2+}} \quad \ldots\ldots\ldots \text{ fast}$$

$$\mathrm{MePH_2^{2+} \xrightarrow{k} Products} \quad \ldots\ldots \text{ slow}$$

The Brønsted rate equation for this mechanism is

$$\text{rate} = k[\mathrm{MePH_2^{2+}}]f_{\mathrm{MePh_2^{2+}}}/f_{\mathrm{tr}^{2+}} = k_1[\mathrm{MePH^+}] \quad . \; . \; . \; . \quad (5)$$

where $f_{\mathrm{tr}^{2+}}$ is the activity coefficient of the transition state complex. From eqn. (5) it may easily be shown that

$$\log k_1 + H_+ = \text{constant} \quad . \; . \; . \; . \; . \; . \; . \quad (6)$$

where H_+ is the Hammett [9] acidity function and the ratios $f_{\mathrm{BH_2^{2+}}}/f_{\mathrm{BH^+}}$ and $f_{\mathrm{MePh^+}}/f_{\mathrm{tr}^{2+}}$ are functions of the solvent only, such that their product is unity. As no data for H_+ are available for the acid range under discussion, eqn. (6) cannot be tested directly.

It is however possible that H_+ and H_0 are identical or differ by a small constant (Michaelis and Granick [10], Brand, Horning, and Thornley,[7] and Bonner and Lockhart [11]). If in fact this is so (*i.e.*, from the definition of H_0 and H_+, $f_{\mathrm{BH^+}} . f_{\mathrm{BH^+}}/f_{\mathrm{BH_2^{2+}}} . f_{\mathrm{B}} = \text{constant}$) then

$$\log k_1 + H_0 = \text{constant} \quad . \; . \; . \; . \; . \; . \; . \quad (7)$$

The slope of a plot of log k_1 against H_0 (Fig. 2) is $-1{\cdot}5$. Thus eqn. (7) does not hold and some other correlation of k_1 with acidity is needed.

There are two bimolecular mechanisms which may be considered for the denitration. These may be written

$$(a) \quad \mathrm{MePH^+ + HA \rightleftharpoons MePH_2^{2+} + A}$$

$$\mathrm{MePH_2^{2+} + A \longrightarrow Products}$$

$$(b) \quad \mathrm{MePH^+ + HA \xrightarrow{k} Products}$$

HA is any solvent acid (either H_3O^+ or H_2SO_4 or both entities) and A is any solvent base (H_2O,HSO_4^-) (cf. Schubert and Zahler [12]). Since for either mechanism the same rate expression may be derived it is possible to consider (*b*) only.

If H_2SO_4 is the effective acid then from (*b*) the rate equation is

$$\text{rate} = k\mathrm{MePH^+})(\mathrm{H_2SO_4})/f_{\mathrm{tr}^+} \quad . \; . \; . \; . \; . \; . \quad (8)$$

Alternatively for H_3O^+ the effective acid,

$$\text{rate} = k(\mathrm{MePH^+})(\mathrm{H_3O^+})/f_{\mathrm{tr}^{2+}}$$

and if $K_{\mathrm{H_2O}}$ is the constant for the equilibrium,

$$\mathrm{H_2O + H^+ \rightleftharpoons H_3O^+}$$

$$\text{rate} = k\, K_{\mathrm{H_2O}}(\mathrm{MePH^+})(\mathrm{H_2O})h_0 f_{\mathrm{BH^+}}/f_{\mathrm{B}} . f_{\mathrm{tr}^{2+}} \quad . \; . \; . \; . \quad (9)$$

where $H_0 = -\log_{10} h_0$ (Hammett [9]).

For both H_2SO_4 and H_3O^+ the expression for the reaction rate becomes

$$\text{rate} = (k'/f_{\mathrm{tr}^+})(\mathrm{MePH^+})(\mathrm{H_2SO_4}) + (k''/f_{\mathrm{tr}^{2+}})(\mathrm{MePH^+})(\mathrm{H_3O^+}) \quad . \quad (10)$$

[9] Hammett, " Physical Organic Chemistry," McGraw Hill Book Co., New York, 1st edn., 1940, p. 267.

[10] Michaelis and Granick, *J. Amer. Chem. Soc.*, 1942, **64**, 1861.

[11] Bonner and Lockhart, unpublished work.

[12] Schubert and Zahler, *ibid.*, 1954, **76**, 1.

In eqns. (8), (9), and (10) f_{tr^+} and $f_{tr^{2+}}$ represent the activity coefficients of transition state complexes. By equating $k_1[\mathrm{MePH^+}]$, the empirical value for the reaction rate, with each of the rates in eqns. (8), (9), and (10), the following corresponding equations may be derived :

$$\log k_1 - \log (\mathrm{H_2SO_4}) = \text{constant} \qquad . \; . \; . \; . \; . \quad (11)$$

$$\log k_1 + H_0 - \log (\mathrm{H_2O}) = \text{constant} \qquad . \; . \; . \; . \; . \quad (12)$$

$$\log k_1 - \log (\mathrm{H_2SO_4}) + H_0 - \log (\mathrm{H_2O}) = \text{constant} \qquad . \; . \; . \quad (13)$$

provided that the appropriate activity coefficient ratios remain constant.

Values of H_0, log (H_2O), and log (H_2SO_4) are thus required for the acid range 71·7—81·3% sulphuric acid at 25°. H_0 may be obtained from Hammett's data,[9] log (H_2O) from a paper by Gold and Hawes [13] and log (H_2SO_4) from Abel's results.[14] In Table 5 the summations in equations (11), (12), and (13) are given.

TABLE 5.

% H_2SO_4	81·30	79·36	78·47	77·58	75·34	71·70
log k_1	−1·29	−1·60	−1·77	−1·98	−2·43	−3·15
log (H_2SO_4)	7·72	7·46	7·34	7·18	6·81	6·27
H_0	−7·02	−6·73	−6·62	−6·51	−6·20	−5·75
log (H_2O)	−2·40	−2·18	−2·08	−1·99	−1·82	−1·49
log k_1 − log (H_2SO_4)	−9·01	−9·06	−9·11	−9·16	−9·24	−9·42
log k_1 + H_0 − log (H_2O)	−5·91	−6·15	−6·31	−6·50	−6·81	−7·41
log k_1 − log (H_2SO_4) + H_0 − log (H_2O)	−13·63	−13·61	−13·65	−13·68	−13·62	−13·68

It is evident from the constancy of the values in the last row of Table 5 that eqn. (13) holds for the denitration.

A termolecular reaction mechanism is not considered as although a rate expression can be derived (cf. Schubert and Zahler [12]) no quantitative relation can be obtained and no reliable inference is possible.

Variation of k_1 *with Methylnitroguanidine Concentration.*—In the above discussion, the effect of the initial methylnitroguanidine concentration on the velocity constant, k_1, was not considered. In fact there is a slight decrease in k_1 with increasing molarity of reagent, as the figures in Table 6 show. This decrease might be attributed to : (*a*) a simple dilution effect ; (*b*) reduction of the acidity of the medium by the methylnitroguanidine ; the previous section has shown that k_1 decreases with decreasing acid strength ; or (*c*) a change in the ionic strength.

TABLE 6. *Influence of initial methylnitroguanidine concentration at 25°.*

Expt. No.	% H_2SO_4	Initial [MeP] [a]	k_1 [b]	k_1, mean [b]	Conversion [c]	K [d]	K, mean [d]	k_2 [e]
83	79·36	0·02	0·0254	0·0252	40·8	177·8	178	4·49
84	,,	,,	0·0251	—	40·6	179·6	—	—
85	,,	0·04	0·0235	0·0230	31·9	167·7	168	3·86
86	,,	,,	0·0225	—	31·8	168·6	—	—
78	78·47	0·02	0·0173	0·0174	44·6	139·2	138	2·37
79	,,	,,	0·0175	—	44·9	137·1	—	—
87	,,	0·05	0·0147	0·0151	32·3	130·2	128	1·93
88	,,	,,	0·0155	—	32·6	126·6	—	—
99	,,	0·10	0·0131	0·0134	25·2	118·2	120	1·61
90	,,	,,	0·0137	—	24·8	122·0	—	—
100	,,	0·20	0·0132	0·0132	20·5	95	95	1·25

[a] mole l.$^{-1}$. [b] min.$^{-1}$. [c] Conversion into methylguanidine at equilibrium, % w/w. [d] l. mole^{-1}. [e] l. mole^{-1} min.$^{-1}$.

It is probable that (*b*) is an important factor as salts such as ammonium sulphate have a marked effect on the acidity of sulphuric acid (Williams and Bevan [15]).

---

[13] Gold and Hawes, *J.*, 1951, 2102.

[14] Abel, *J. Phys. Chem.*, 1946, **50**, 260 ; 1948, **52**, 908.

[15] Williams and Bevan, *Chem. and Ind.*, 1955, 171.

Effect of Temperature upon Denitration.—Results for the effect of a 20° rise in temperature are given in Table 7. The Arrhenius equations for 77·58 and 75·35% sulphuric acid are, respectively, $k_1 = 6{\cdot}1 \times 10^{11} \exp(-21{,}200/\boldsymbol{R}T)$ and $k_1 = 4{\cdot}0 \times 10^{11} \exp(-21{,}500/\boldsymbol{R}T)$ l. mole^{-1} sec.$^{-1}$.

Comparison with Denitration of Nitroguanidine.—The denitration of methylnitroguanidine is four times as fast as that for nitroguanidine. As the methyl group is electron donating, this result is consistent with either of the bimolecular reaction mechanisms (*a*) and (*b*), and thus cannot be used to distinguish between them.

Nitration of Methylguanidine.—In two media nitration of methylguanidine was shown to follow the rate equation,

$$d[\mathrm{MePH^+}]/dt = k_2[\mathrm{MeGH^+}][\mathrm{HNO_3}]$$

Velocity constants for nitration, k_2, calculated directly from a reversible kinetic equation [8] are given in Table 1. They may also be obtained indirectly from the denitration velocity measurements since for such reactions the velocity constant for the reverse nitration is given by $k_2 = Kk_1$, where K is the equilibrium product defined in eqn. (14). Velocity constants thus derived are given in Tables 4 and 6. log k_2 is a linear function of the acidity function J_0 (Williams and Bevan,[15] Gold and Hawes,[13] and Gold [16]) and its theoretical equivalent C_0 (Deno, Jaruzelski, and Schriesheim [17]). The slopes of the respective plots are $-0{\cdot}93$ (Fig. 2) and $-1{\cdot}2$. This confirms the nitronium ion mechanism for the nitration of methylguanidine.

TABLE 7. *Variation of temperature.*

(Initial methylnitroguanidine 0·02000M.)

Expt. No.	% H_2SO_4	Temp.	k_1 (min.$^{-1}$)	k_2 (l. mole^{-1} min.$^{-1}$)	K (l. mole^{-1})
112	77·58	14·96°	0·00311	0·5037	166·5
113	,,	,,	0·00292	—	167·1
108	,,	24·92	0·01043	1·122	107·0
109	,,	,,	0·01048	—	107·6
110	,,	34·98	0·0334	2·141	64·7
111	,,	,,	0·0328	—	64·7
80	75·35	24·90	0·00370	0·2303	62
81	,,	,,	0·00373	—	—
114	,,	34·98	0·0122	0·4928	40·4
115	,,	45·13	0·0376	1·060	28·2

The effect of a 20° rise in temperature on k_2 is shown in Table 7. The Arrhenius equations for 77·58 and 75·35% sulphuric acid are, respectively, $k_1 = 4{\cdot}40 \times 10^7 \exp(-12{,}800/\boldsymbol{R}T)$ and $k_1 = 1{\cdot}16 \times 10^8 \exp(-14{,}300/\boldsymbol{R}T)$.

The Methylnitroguanidine–Methylguanidine Nitrate Equilibrium.—It is convenient to express the results of the concentrations found at equilibrium for solutions of methylnitroguanidine in sulphuric acid in terms of the equilibrium product, K, defined in eqn. (14), since it is similar to a product used by Simkins and Williams [1] for nitroguanidine:

$$K = [\mathrm{MePH^+}]_e/[\mathrm{MeGH^+}]_e[\mathrm{HNO_3}]_e \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

The influence of initial methylnitroguanidine concentration and medium composition on K is given in Tables 6 and 8 for the range 71·7—99·1% sulphuric acid. In 99% sulphuric acid the values quoted are only approximate as the heat of solution caused some decomposition of the methylnitroguanidine.

In Table 1 values of K for two media are compared with the theoretically equivalent $K' = k_2/k_1$.

The variation in K is very similar to that found for nitroguanidine and the optimum condition for nitration is again in 88% sulphuric acid.

If the equilibrium is represented by the equation

$$\mathrm{MeGH^+} + \mathrm{NO_2^+} + \mathrm{HSO_4^-} \rightleftharpoons \mathrm{MePH^+} + \mathrm{H_2SO_4} \quad . \quad . \quad . \quad (15)$$

---

[16] Gold, *J.*, 1955, 1263.

[17] Deno, Jaruzelski, and Schriesheim, *J. Amer. Chem. Soc.*, 1955, **77**, 3044.

then it may be shown,[1] for $[NO_2OH] \gg [NO_2^+]$, that log K should be connected with log (H_2O) by a straight line of slope —1 if $f_{NO_2\cdot OH}$ does not vary greatly. For acids in which the nitronium-ion concentration is small, namely those of less than 85% sulphuric acid, the slope of a plot of log K against log $(p/p_0)_{H_2O}$ (Gold and Hawes [13]) is 1·16 (Fig. 3).

FIG. 2.

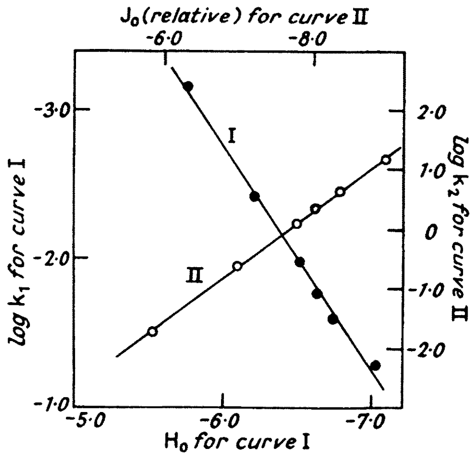
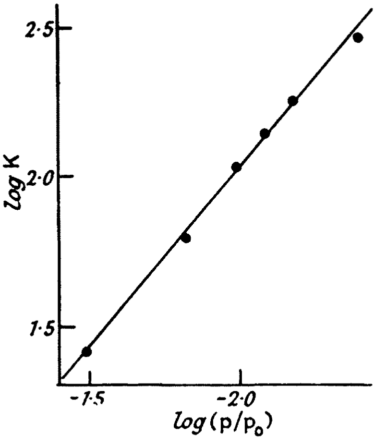


FIG. 3.



For acids containing more than 85% sulphuric acid Simkins and Williams [1] have suggested that K/rQ = constant, in which $r = [HSO_4^-]/[H_2SO_4]$ and $Q = [NO_2^+]/[HNO_3]$. Values of K/rQ are given in Table 9 and are calculated by Simkins and Williams's method

TABLE 8. *Influence of the composition of the medium on equilibrium positions at* 25°.

Expt. No.	% H_2SO_4	Conversion into methylguanidine % w/w	Conversion into methylguanidine mean % w/w	K (l. mole⁻¹)	Mean K (l. mole⁻¹)
(Initial concentration of methylnitroguanidine, 0·02000M.)					
121	99·1	94·9	94	2·8	3·4
122	,,	93·0		4·0	
47	99·0	91·7	92	4·9	4·7
48	,,	92·3		4·5	
75	96·25	80·5	80·4	15·6	15·4
77	,,	80·3		15·3	
68	94·64	68·7	68·2	34·3	34·8
69	,,	67·7		35·3	
72	93·28	51·8	51·8	89·8	89·7
73	,,	51·9		89·6	
66	89·93	25·2	25·4	590	580
67	,,	25·7		565	
43	89·43	22·3	22·2	781	790
44	,,	22·5	—	770	—
63	,,	21·9	—	810	—
64	,,	22·5	—	783	—
65	,,	21·9	—	818	—
74	87·58	18·9	19·0	1135	1120
76	,,	19·2		1103	
41	84·10	24·8	25·1	611	596
42	,,	25·4		581	
(Initial concentration of methylnitroguanidine, 0·02000M.)					
49	81·30	33·7	33·7	292	291
71	,,	33·8		290	
83	79·36	40·8	40·7	177·8	178
84	,,	40·6		179·6	
78	78·47	44·6	44·7	139·2	138
79	,,	44·9		137·1	
108	77·58	48·9	48·8	107·0	107·3
109	,,	48·8		107·6	
80	75·34	58·0	58·0	62·2	62·2
124	71·70	73·0	72·8	25·6	25·7
125	,,	72·7		25·9	
(Initial concentration of methylnitroguanidine, 0·2000M.)					
92	83·78	12·1	12·6	302	275
93	,,	13·2		249	
95	80·78	16·0	15·9	164·1	166
101	,,	15·8		167·4	
106	78·84	20·15	20·5	98·3	94
107	,,	20·9		90·1	
100	78·47	20·5	20·5	95·1	95

TABLE 9.

% H_2SO_4	99·1	99·0	96·25	94·64	93·28	89·93	89·43	87·58
Q	1	1	1	0·96	0·94	0·64	0·56	0·23
K (l. mole⁻¹)	3·4	4·7	15·4	34·8	89·7	580	790	1120
r	19·27	17·21	3·73	2·24	1·57	0·65	0·58	0·37
K/rQ (l. mole⁻¹)	65·5	80·9	57·4	81·3	151	589	818	1802

except that for 87—89% sulphuric acid *r* was obtained by assuming the mole fraction equilibrium constant for the reaction

$$H_2O + H_2SO_4 = H_3O^+ + HSO_4^-$$

to be 50 (Deno and Taft [20]).

It is evident that K/rQ is by no means constant except over the range 94—99% sulphuric acid, and for this range estimates of K are least accurate since the percentage denitration is large and also the ratio $[H_2SO_4]/[HSO_4^-]$ increases very rapidly and may thus be in error.

Ionisation of methylguanidine to a doubly charged ion in concentrated acids cannot be the cause of variation in values of K/rQ as cryoscopic results on guanidine salts show that such a factor is negligible for guanidine [8] and it may be assumed to be the same for methylguanidine (Angyal and Warburton [21] have shown that methylguanidines are equally basic).

Effect of Temperature on Equilibrium Product.—The results for the effect on K of a temperature rise of 20° for two media are given in Table 7. Log K is linearly related to $1/T$ for both media.

Comparison with Equilibrium Position of Nitroguanidine.—For 0·2M-solutions of methylnitroguanidine, the equilibrium position is the same, within the limits of experimental error, as for 0·2M-solutions of nitroguanidine. This is illustrated in Fig. 4 in which the percentage denitration at equilibrium for both compounds is plotted against sulphuric acid composition.

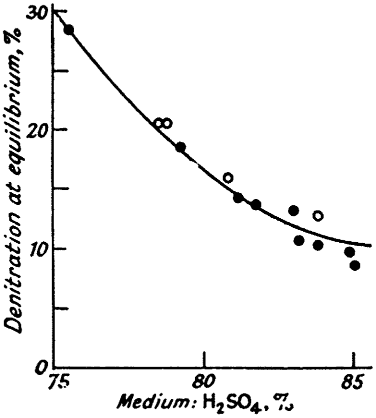


FIG. 4.

● 0·2M-*Nitroguanidine.*[1]
○ 0·2M-*Methylnitroguanidine.*

Note on NN'*-Dimethyl-*N''*-nitroguanidine.*—Before methylnitroguanidine was chosen for investigation, the possibility of using *NN'*-dimethyl-*N''*-nitroguanidine was examined. Davis and Elderfield [22] had tried to prepare it by the nitration in sulphuric acid of *NN'*-dimethylguanidine and although similar conditions gave good yields of nitroguanidine, methylnitroguanidine, and certain other alkylnitroguanidines, they proved ineffective for the *NN'*-dimethyl compound and also for the *NN'N''*-trimethyl compound. The presence of two alkyl groups on different nitrogen atoms apparently completely inhibited nitration. Such a compound, if obtained by some other route, would thus be ideal for denitration studies, provided that it did not decompose under acid conditions. Unfortunately no suitable method of preparation of the *NN'*-dimethyl compound presented itself. The only report of the preparation of similar compounds was by treatment of 4 : 5-dihydro-2-nitramino-1-nitrosoglyoxaline with an alkylamine [23] and yields were then exceedingly low (0·4% for the dimethyl compound).

[18] Bennett, Brand, and Williams, *J.*, 1946, 869.
[19] Bonner and Williams, *Chem. and Ind.*, 1951, 820.
[20] Deno and Taft, *J. Amer. Chem. Soc.*, 1954, **76**, 244.
[21] Angyal and Warburton, *J.*, 1951, 2492.
[22] Davis and Elderfield, *J. Amer. Chem. Soc.*, 1933, **55**, 731.
[23] McKay, *Chem. in Canada*, 1951, **3**, 21; *J. Org. Chem.*, 1951, **16**, 1395; *ibid.*, p. 1846; *Canad. J. Chem.*, 1953, **31**, 284.

It was thought possible that in the treatment of nitroguanidine with an alkylamine, the dialkylated compound would also be produced, though in no instance had an *NN'*-di-alkyl-*N''*-nitroguanidine been reported as having been obtained by this method.[24-26] Hence the reaction of methylamine with nitroguanidine was examined with care, and a very small yield of *NN'*-dimethyl-*N''*-nitroguanidine obtained. The method was not, however, practicable for large-scale preparation and since methylations by other means (diazomethane,[27] dimethyl sulphate) were not successful *NN'*-dimethyl-*N''*-nitroguanidine was not used for a full kinetic investigation.

One denitration of *NN'*-dimethyl-*N''*-nitroguanidine was, however, carried out in 78·47% sulphuric acid. The technique employed was the same as that used for the monomethyl compound. It was assumed that the ultraviolet spectra in dilute acid and in water were the same, as this was true for the monomethyl compound. Values of the rate constant, k_1 (obtained from a reversible kinetic equation), the equilibrium product, K, and the rate constant for the reverse reaction, $k_2 = Kk_1$, are given below, together with corresponding results for methylnitroguanidine.

Medium, 78·47% H_2SO_4. Temp. 25°.

	k_1 (min.$^{-1}$)	K (l. mole^{-1})	k_2 (l. mole^{-1} min.$^{-1}$)	Denitration at equil., %
Methylnitroguanidine	0·0166	138·2	2·29	44·6
NN'-Dimethyl-*N''*-nitroguanidine	0·0248	7·95	0·197	87·7

The increase in denitration rate, due to the addition of a second electron-donating methyl group, is in accord with the bimolecular reaction mechanism. The velocity of nitration of the dimethyl compound is however considerably less than the velocity of nitration of the monomethyl compound. This decrease is peculiar since addition of one methyl group to the guanidine molecule increased the nitration reaction velocity by a factor of 3—4. It suggests that the presence of two methyl groups, each on different nitrogen atoms sterically hinders the approach of a nitronium ion to the third nitrogen atom.

EXPERIMENTAL

Materials.—Methylnitroguanidine, m. p. 160—161° (Found : C, 20·5; H, 5·1; N, 47·9. Calc. for $C_2H_6O_2N_4$: C, 20·3; H, 5·1; N, 47·5%), was made from methylamine hydrochloride and nitroguanidine (McKay and Wright[28]). Methylguanidine sulphate, m. p. 238·5° (Found : C, 20·3; H, 6·5; N, 35·3. Calc. for $C_4H_{16}O_4N_6S$: C, 19·7; H, 6·6; N, 34·4%), was a commercial specimen recrystallised from 80% ethanol. Methylguanidine nitrate, m. p. 149—149·5° (Found : C, 18·3; H, 6·1; N, 41·8. Calc. for $C_2H_8O_3N_4$: C, 17·6; H, 5·9; N, 41·2%), was made by treatment of the sulphate with barium nitrate and was recrystallised from anhydrous ethanol.

NN'-Dimethyl-*N''*-nitroguanidine was prepared as follows: Nitroguanidine (20·8 g.) was added to a solution of potassium hydroxide (24 g.) in water (60 ml.). The stirred solution was warmed to 40° and methylammonium chloride (27 g.) was added during 5 min. as soon as effervescence from the decomposing nitroguanidine was observed (3½ min. from initial addition of nitroguanidine). The temperature rose to 51° during the addition of methylammonium chloride, and was raised to 61° during the 15 min. following the addition. The temperature was maintained at 60—61° and the solution stirred for a further 15 min. The solution was then cooled, and the precipitate of methylnitroguanidine (10·0 g.) filtered off.

The filtrate was heated to 50—70° for 30 min. and then kept in a refrigerator for 44 hr. The long thin crystals were filtered off, washed with water, and dried at 70°. They gave positive Franchimont tests with diphenylaniline and dimethylaniline. The crystals were recrystallised once from 95% alcohol and twice from water. The product (0·55 g.) had m. p. 171° (Found : C, 27·8; H, 6·1; N, 42·2%. Calc. for $C_3H_8O_2N_4$: C, 27·3; H, 6·1; N, 42·4%).

Sulphuric acid media were standardised by Simkins and Williams's method.[1] A medium

---

[24] Davis and Luce, *J. Amer. Chem. Soc.*, 1927, **49**, 2303.
[25] McKay and Wright, *ibid.*, 1948, **70**, 430.
[26] McKay, *Chem. Reviews*, 1952, **51**, 314.
[27] Kirkwood and Wright, *J. Org. Chem.*, 1953, **18**, 629.
[28] McKay and Wright, *J. Amer. Chem. Soc.*, 1947, **69**, 3028.

containing nitric acid was prepared from anhydrous nitric acid and analysed by Treadwell and Vontobel's method.[29]

Measurements of Reaction Velocity and Equilibrium Composition.—A weighed quantity of the sulphuric acid was placed in a 50 or 100 ml. flask, brought to the temperature of the thermostat, and a known quantity of methylnitroguanidine or methylguanidine nitrate added from a B19 socket cap. The flask was shaken and kept in the thermostat. The time for dissolution of the guanidine varied with both medium and reagent concentration and was of the order of 1—4 min. Samples (1 ml. or, usually, 2 ml.) were withdrawn at intervals and were run into about 100 ml. of water which was subsequently made up to 250 ml. with distilled water, and an aliquot part diluted quantitatively to a strength of <0·16N-sulphuric acid so that it could be analysed for methylnitroguanidine.

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

Analytical Method.—The samples were analysed for methylnitroguanidine by means of the ultraviolet absorption spectrum; this was simpler than analysis for nitrate ion.

In aqueous solution methylnitroguanidine has an ultraviolet absorption spectrum similar to that of nitroguanidine,[6] with $\varepsilon_{\text{max.}}$ 14,040 at 2670—2675 Å, and although this peak decreases with a large increase in acidity, the value for solutions in 0—0·16N-sulphuric acid is constant within the experimental error (cf. Table 10). From these figures the maximum extinction coefficient for methylnitroguanidine, in 0—0·16N-acid, was taken as 14,040 at 24°.

TABLE 10. $\varepsilon_{\text{max.}}$ *at* 2670—2675 Å *for methylnitroguanidine in* 0—0·5N-*sulphuric acid.*

Sulphuric acid, N	0·00	0·00	0·05	0·10	0·16	0·20	0·40	0·50
Temp.	21°	24°	23°	24°	24°	20°	20°	23°
$\varepsilon_{\text{max.}}$	14,080	14,040	14,080	14,030	14,030	14,060	13,880	13,710

The optical density varied slightly with temperature as Table 11 shows. It was thus necessary during optical-density measurements to control the temperature of the absorbing solution; the range 23—25° was used.

TABLE 11. *Variation of optical density, D, with temperature, at* 2670 Å.

Temp.	15°	16°	17°	18°	19°	20°	21°	22°	23°	24°	25°	26°
Expt. 1	0·886	0·887	0·886	—	0·884	0·882	—	—	—	—	—	—
Expt. 2	—	—	—	—	1·106	1·106	1·105	1·104	—	—	—	—
Expt. 3	—	—	—	—	0·826	0·825	—	0·824	—	0·823	0·822	0·821
Expt. 4	0·799	—	—	—	—	—	—	—	0·796	—	—	—

The solutions obeyed Beer's law over the concentration range 2—7 × 10^{-5}M-methylnitroguanidine and there was no alteration in the optical density, *D*, of a solution during a period of 3 days. Solutions of methylnitroguanidine in sulphuric acid, strength <0·16N, could thus be analysed by absorption measurements.

Tests of Method.—Solutions of methylnitroguanidine in 50% and 40% H_2SO_4 were analysed under conditions corresponding to a denitration experiment. The mean error of the results was ±0·5% for measurements in 50% sulphuric acid and ±0·3% for measurements in 40% sulphuric acid; the latter were obtained after some velocity measurements had been made and the technique improved.

Diluted samples of a denitration reaction could be kept for several days without alteration in light absorption.

The other molecular species produced during denitration, namely nitric acid and methylguanidine, have very slight absorption in aqueous solution at 2670 Å and provided that the denitration of methylnitroguanidine did not exceed 95% this absorption could be neglected in calculating the concentration of methylnitroguanidine.

Absorption Measurements.—These were made with a Hilger "Uvispek" photoelectric spectrophotometer, 1·000 cm. quartz cells being used.

The author gratefully acknowledges the help received from the late Professor Gwyn Williams who suggested the subject for research and thanks Dr. T. G. Bonner for useful discussion.

ROYAL HOLLOWAY COLLEGE (UNIVERSITY OF LONDON),
ENGLEFIELD GREEN, SURREY.
[*Present Address*: ROYAL COLLEGE OF SCIENCE AND TECHNOLOGY, GLASGOW.]

[*Received, July 9th*, 1956.]

---

[29] Treadwell and Vontobel, *Helv. Chim. Acta*, 1937, **20**, 573.