783. *The Denitration of Nitroguanidines in Strong Acids. Part I. The Correlation of Rate Constants with the Acidity Function, H_0, and Activities of Solvent Entities.*

By T. G. Bonner and J. C. Lockhart.

The rates of denitration of some nitroguanidines have been measured in an extensive range of strongly acidic media, and a difference in mechanism has been detected in sulphuric acid and perchloric acid. The empirical relation between rate constant, the acidity function H_0, and the activities of solvent species previously reported [1] for the denitration of *N*-methyl-*N'*-nitroguanidine in sulphuric acid has been confirmed for several other nitroguanidines and a new interpretation of this relation put forward. The occurrence of a minimum in the extent of denitration at equilibrium confined to the range 85—88% sulphuric acid for all the nitroguanidines investigated is discussed.

Nitration of guanidine in concentrated aqueous acid solution is reversible,[2] and rates of the reverse reaction, *i.e.*, denitration, were first obtained by Simkins and Williams.[3] Reliable measurements of the denitration rate were limited by an unfavourable equilibrium position but *N*-methyl-*N'*-nitroguanidine gave [1] accurately measurable rates in the range 71—81% of sulphuric acid. These investigations established that denitration is a first-order reaction (opposed by the second-order nitration). A parallelism was found [1, 3] between the rate of the nitration and the ionisation of triarylmethanols in the same range of media which established that the nitrating entity was the nitronium ion.[4] The importance of the part played by the solvent in these equilibria is shown by the occurrence of a minimum in the extent of denitration of nitroguanidine and its *N*-methyl derivative in the same medium, *viz.* 88% sulphuric acid.

Since nitroguanidine and its *N*-methyl derivative are completely converted into their conjugate acids in below 40% sulphuric acid and are quite stable at very much higher acidities, it was assumed that denitration took place only after the addition of a second proton.[1] The mechanism first suggested [2] represented the denitration as a rate-determining ejection of the nitronium ion from the doubly-charged nitroguanidine cation

$$PH^+ + H^+ \overset{\text{fast}}{\rightleftharpoons} PH_2^{++} \overset{\text{slow}}{\rightleftharpoons} GH^+ + NO_2^+$$

where P and G represent nitroguanidine and guanidine, respectively. The species PH_2^{++} can only be present in relatively minute amount but the extent of its formation is difficult to assess. It has been shown that the stronger base, guanidine, forms detectable amounts of its doubly protonated derivative only in sulphuric acid stronger than 99% [5] but urea, a base of similar strength to nitroguanidine, does appear to become doubly charged in concentrated sulphuric acid.[6] The essential point, however, is whether the reaction proceeds uniquely through this species. This can be tested over the range of media studied by means of a relation of the type

$$\log k + H_0 = \text{constant} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where k is the rate constant for denitration and H_0 is Hammett's acidity function.[7] Since the reactant is envisaged as carrying two positive charges, the acidity function required is

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[1] Hardy-Klein, *J.*, 1957, 70.

[2] (*a*) Simkins and Williams, *J.*, 1952, 3086; (*b*) Holstead, Lamberton, and Wyatt, *J.*, 1953, 3341; (*c*) Holstead and Lamberton, *J.*, 1953, 3349.

[3] Simkins and Williams, *J.*, 1953, 1386.

[4] Westheimer and Kharasch, *J. Amer. Chem. Soc.*, 1946, **68**, 1871.

[5] Williams and Hardy, *J.*, 1953, 2560.

[6] Hammett, "Physical Organic Chemistry," McGraw Hill Book Co., New York, 1st Edn., 1940, p. 47.

[7] *Idem, ibid.*, p. 267.

H_+ rather than H_0 but in the absence of a scale of H_+ values similar to that evaluated by Hammett for H_0, the relation can be tested only with the latter. This is acceptable, since it has been recently established that H_0 and H_+ are parallel functions of medium composition over a wide range of sulphuric acid–water mixtures.[8] The test of the mechanism proposed is that the plot of log k against H_0 should be a straight line of slope -1. In fact, the slopes so far reported have been considerably removed from -1, being $-1{\cdot}42$ for nitroguanidine[3] and $-1{\cdot}50$ for *N*-methyl-*N*′-nitroguanidine. Bimolecular reactions were considered,[1] similar to those suggested for decarbonylation of alkylbenzaldehydes in sulphuric acid,[9] but no simple bimolecular mechanism appeared to be operative. A useful

TABLE 1. *Denitration in sulphuric acid–water at* 25° (initial concn. 0·01M; k in 10^3 min.$^{-1}$).

% H_2SO_4	A	B	2-Nitramino-1 : 3 : 4-triazole			2-Nitrimino-1 : 3-diaza*cyclo*hexane			*NN*-Dimethyl-*N*′-nitroguanidine		
			k	C	D	*k*	C	D	*k*	C	D
67·0	4·36	9·52	0·42	8·80	13·16	—	—	—	—	—	—
68·0	4·46	9·67	—	—	—	0·274	8·77	13·23	—	—	—
69·7	4·59	10·03	—	—	—	0·546	8·70	13·31	0·468	8·81	13·40
70·5	4·67	10·28	1·13	8·56	13·23	0·834	8·69	13·36	—	—	—
71·8	4·78	10·54	2·09	8·44	13·22	—	—	—	—	—	—
72·8	4·84	10·76	—	—	—	2·84	8·48	13·33	1·84	8·65	13·49
74·8	4·98	11·14	12·43	8·07	13·29	7·38	8·29	13·29	4·37	8·52	13·50
76·1	5·08	11·41	—	—	—	11·8	8·29	13·39	—	—	—
78·6	5·24	11·91	63·0	7·87	13·11	36·4	8·12	13·36	—	—	—
70·2	5·27	12·05	—	—	—	—	—	—	36·4	8·22	13·49
81·9	5·33	12·45	—	—	—	—	—	—	121	8·04	13·37

% H_2SO_4	A	B	4-Methyl-2-nitrimino-1 : 3-diaza*cyclo*pentane			2-Nitrimino-1 : 3-diaza*cyclo*pentane *		
			k	C	D	*k*	C	D
76·1	5·08	11·41	0·514	9·62	14·70	0·302	9·84	14·92
78·6	5·24	11·91	—	—	—	1·33	9·54	14·78
79·2	5·27	12·05	1·86	9·49	14·76	—	—	—
81·2	5·33	12·37	5·16	9·33	14·66	3·99	9·34	14·7$_6$
81·9	5·33	12·45	5·95	9·36	14·69	5·98	9·34	14·6$_7$
83·3	5·38	12·72	13·6	9·21	14·60	12·07	9·27	14·6$_5$
85·1	5·42	12·99	26·0	9·15	14·57	24·3	9·20	14·6$_2$
87·5	5·40	13·31	91·9	8·95	14·35	74·0	9·04	14·4$_4$
89·9	5·30	13·51	—	—	—	191·1	8·93	14·2$_3$
92·6	5·10	13·57	—	—	—	526	8·75	13·85

A = log $\{H_2SO_4\}$ + log $\{H_2O\}$; B = $-(H_0 - \log\{H_2SO_4\} - \log\{H_2O\})$; C = $-(\log k + H_0)$; D = $-(\log k + H_0 - \log\{H_2SO_4\} - \log\{H_2O\})$.

* Initial concn. 0·008M.

Values of log $\{H_2SO_4\}$ were obtained from Abel, *J. Phys. Chem.*, 1946, **50**, 260; 1948, **52**, 908, and of log $\{H_2O\}$ from Gold and Hawes, *J.*, 1951, 2102.

TABLE 2. *Denitration in aqueous perchloric acid and in sulphuric acid–acetic acid at* 25° (initial concn. 0·01M; k in 10^3 min.$^{-1}$).

Perchloric acid–water			Sulphuric acid–acetic acid	
% $HClO_4$	*N*-methyl-*N*′-nitroguanidine *k*	2-nitrimino-1 : 3-diaza*cyclo*hexane *k*	% H_2SO_4	2-nitrimino-1 : 3-diaza*cyclo*hexane *k*
59·6	0·038	0·186	52·7	0·736
63·6	—	1·67	55·8	0·894
64·6	0·316	3·46	59·1	1·50
66·4	2·02	—	64·6	2·07
67·0	—	12·7	65·5	3·78
69·0	10·2	—	71·1	10·5
72·0	63·2	—	—	—

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[8] Bonner and Lockhart, *J.*, 1957, 364.

[9] Schubert and Zahler, *J. Amer. Chem. Soc.*, 1954, **76**, 1; Schubert, Donohue, and Gardner, *ibid.*, p. 9; Schubert, Zahler, and Robins, *ibid.*, 1955, **77**, 2293.

empirical relation, however, was found[1] in the reasonable constancy over the range 71—82% sulphuric acid of the summation of terms in equation (2)

$$\log k + H_0 - \log \{H_2O\} - \log \{H_2SO_4\} = \text{constant} \quad . \quad . \quad . \quad (2)$$

where the quantities in braces represent activities. Considerable difficulty is apparent in the attempts to reconcile equation (2) with a simple mechanism of denitration.[10]

It appeared desirable to examine denitration of other substituted nitroguanidines with sufficient variety of structure to ensure an extension of the range of acidity over which the reaction takes place, and also to employ strongly acid media other than aqueous sulphuric acid. A few compounds (detailed in Table 1) were suitable for measurements of rate and equilibria in aqueous sulphuric acid. 2-Nitrimino-1 : 3-diaza*cyclo*hexane (II) and *N*-methyl-*N*′-nitroguanidine were studied in aqueous perchloric acid and the former in anhydrous sulphuric acid–acetic acid also (see Table 2).

EXPERIMENTAL

Materials.—Sulphuric acid and perchloric acid solutions were prepared by dilution of the " AnalaR " acid with distilled water and analysed as previously reported.[2a] 100% Sulphuric acid was obtained from a weak oleum by dilution to maximum freezing point with " AnalaR " sulphuric acid. Sulphuric acid–acetic acid solutions were obtained by mixing the required weights of 100% sulphuric acid and 100% acetic acid.

Nitroguanidine was obtained by nitration of guanidine in sulphuric acid.[11] Methylnitroguanidine, m. p. 160—161°, was made from nitroguanidine as described by McKay and Wright.[12] *NN*′-Dimethyl-*N*″-nitroguanidine, m. p. 171—172°, was obtained from the mother liquor of this reaction by Hardy-Klein's method.[1] *NN*-Dimethyl-*N*′-nitroguanidine, m. p. 194—195°, was made from *N*-methyl-*N*′-nitro-*N*-nitrosoguanidine and dimethylamine.[12]

2-Nitrimino-1 : 3-diaza*cyclo*pentane, m. p. 220—221°, 4-methyl-2-nitrimino-1 : 3-diaza*cyclo*pentane, m. p. 170—171°, and 2-nitrimino-1 : 3-diaza*cyclo*hexane, m. p. 249—250°, were prepared by the method used for methylnitroguanidine.[12] 2-Nitramino-1 : 3 : 4-triazole was made by refluxing formamidonitroguanidine with sodium carbonate.[13]

All these nitroguanidines were purified by recrystallisation to constant spectrum for kinetic work. Spectral data are given in the following paper. A commercial specimen of guanidine nitrate was recrystallised from water, then six times from water containing 10% of alcohol.

Recovery of Denitration Products.—*NN*-Dimethyl-*N*′-nitroguanidine and the diaza-*cyclo*hexane and -*cyclo*pentanes were tested by Holstead and Lamberton's method to demonstrate the formation of nitric acid. The yield in all cases was within 71—73% of theory, as had been previously found for potassium nitrate and nitroguanidine. The nitration mixture from 2-nitrimino-1 : 3-diaza*cyclo*pentane was also treated to yield the guanidine as nitrate,[2b] needles, m. p. 112—113°, identified as 2-amino-1 : 3-diaza*cyclo*pentane nitrate by conversion into the carbonate and picrate.[14]

Measurement of Reaction Velocity and Equilibrium Composition.—The optical density of a sample suitably diluted with water was measured at the absorption maximum for the particular nitroguanidine.

The absorptions of guanidine,[15] alkylguanidines,[1] and 2-aminotetrahydropyrimidine [16] are known to be negligible at 2600—2900 Å. The absorption of 2-amino-1 : 3-diaza*cyclo*pentane nitrate also was found to be negligible in this region. The nitrate ion has an extinction coefficient of ε, 2 in this region and can be neglected [1] as long as denitration is less than 95% complete.

Rate constants were obtained graphically from the kinetic equation previously employed,[1] *i.e.* $kt(2a - x_e) = 2{\cdot}3x_e \log_{10}\{a(x_e - x)/[ax_e + x(a - x_e)]\}$ where a is the initial concentration of reactant, x the concentration of the denitrated reactant at time t, and x_e the concentration

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[10] Hardy-Klein, *J.*, 1957, 3312.

[11] Davis, *Org. Synth.*, Coll. Vol. I, 1948, 399.

[12] McKay and Wright, *J. Amer. Chem. Soc.*, 1947, **69**, 3028.

[13] Henry, *ibid.*, 1950, **72**, 5343.

[14] Stefanye and Howard, *ibid.*, 1955, **77**, 761.

[15] " International Critical Tables," Vol. V, McGraw Hill Book Co., New York, 1929, p. 367.

[16] Hamer, Waldron, and Woodhouse, *Arch. Biochem. Biophys.*, 1953, **47**, 272.

of the latter at equilibrium. A plot of the log term against time was a straight line to about 80% of the conversion for all compounds and media studied.

RESULTS AND DISCUSSION

The Relation between Rate Constant and Acidity Function, H_0.—The rapid increase in rate of denitration with increasing acidity [1,3] was also found for all the compounds in Table 1. Rate constants increase approximately one-hundred fold over a 10% range of acid, for both sulphuric acid and perchloric acid solutions. The influence of acidity is only slightly less marked in sulphuric acid–acetic acid. The plots of log k against H_0 for aqueous sulphuric acid [17] are shown in Fig. 1; the slopes for all the compounds lie between $-1{\cdot}41$ and $-1{\cdot}49$. In aqueous perchloric acid [18] the two compounds studied, 2-nitrimino-1 : 3-diaza*cyclo*hexane and *N*-methyl-*N'*-nitroguanidine, give slopes of $-0{\cdot}97$ and $-1{\cdot}09$, respectively. These results imply that denitration in perchloric acid proceeds through a diprotonated species formed in fractionally small amount [17] but that a more complex reaction occurs in sulphuric acid. Since rates in the latter are faster than required by theory, it is possible that in this medium, (*a*) catalysis occurs by some species not present in aqueous perchloric acid, or (*b*) the transition state of the reactant associates with solvent species in a manner not paralleled by the conjugate acids of the Hammett bases used to evaluate H_0.

FIG. 1. *Variation of* log *k* (*denitration*) *with* H_0.

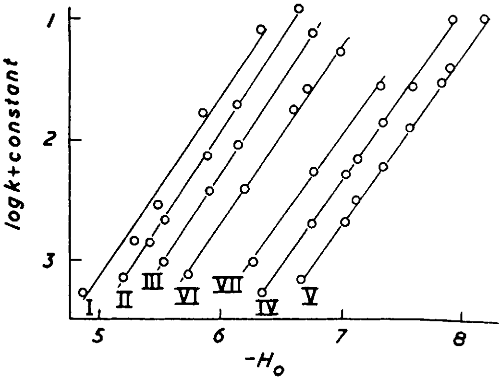
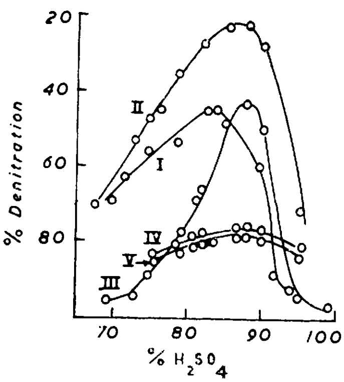


FIG. 2. % *Denitration of equilibrium.*



I, 2-Nitramino-1 : 3 : 4-triazole ($-1{\cdot}44$); II, 2-Nitrimino-1 : 3-diaza*cyclo*hexane ($-1{\cdot}46$); III, *NN*-Dimethyl-*N'*-nitroguanidine ($-1{\cdot}46$); IV, 4-Methyl-2-nitrimino-1 : 3-diaza*cyclo*pentane ($-1{\cdot}41$); V, 2-Nitrimino-1 : 3-diaza*cyclo*pentane ($-1{\cdot}44$); VI, *N*-Methyl-*N'*-nitroguanidine (from ref. 1) ($-1{\cdot}49$); VII, Nitroguanidine (from ref. 3) ($-1{\cdot}46$).

Values in parentheses are of (log k)/H_0.

A mechanism basically similar to that in perchloric acid cannot be excluded for sulphuric acid since previous investigators have often found justification for interpreting slopes of from $-0{\cdot}7$ to $-1{\cdot}5$ in terms of the simple mechanism associated with a slope of -1.[19-22] However, application of the results reported here to equation (2) showed an excellent fit in the range 67—85% sulphuric acid for all the nitroguanidines in Table 1, except 2-nitrimino-1 : 3-diaza*cyclo*pentane. With the latter the constancy is not so marked, but considerable divergence from constancy occurs only above 85% sulphuric

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[17] Hammett and Deyrup, *J. Amer. Chem. Soc.*, 1932, **54**, 2721.

[18] Bonner and Lockhart, *J.*, 1957, 2840.

[19] Long and McIntyre, *J. Amer. Chem. Soc.*, 1954, **76**, 3240; Long and Paul, *Chem. Rev.* 1957, **57**, 935.

[20] Gold and Satchell, *J.*, 1955, 2743, 3619, 3622.

[21] Satchell, *J.*, 1956, 3911.

[22] Gold and Hilton, *J.*, 1955, 843.

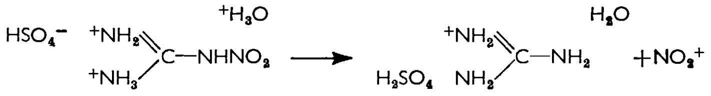
acid. It may be significant that this medium is very close to that corresponding to the 1 : 1 mole ratio of sulphuric acid to water and possibly a change of mechanism occurs at the higher acidities. As the results in Table 1 show, the sum of the terms log $\{H_2SO_4\}$ + log $\{H_2O\}$ increases continuously with acidity as does that of the terms log k and H_0. It is the difference between these two sets of values which remains constant. The constancy of the terms in equation (2) is consistent with a rate constant represented by equation (3)

$$k = \text{constant}\ \{H_2SO_4\}\ \{H^+\}\ \{H_2O\}\, f_B/f_{BH^+} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

and this in turn implies a transition complex formed from a nitroguanidine cation PH^+ and the solvent species H_3O^+ and H_2SO_4. If molecular sulphuric acid is absent from the more aqueous sulphuric acid solutions used for denitration, the same transition complex could equally well be formed from the diprotonated nitroguanidine PH_2^{++} and the solvent species HSO_4^- and H_3O^+, both of which should be present in excess in most, if not all, of the media studied. The absorption spectra indicate that addition of a proton to nitroguanidine occurs at the nitrimino-nitrogen atom (see following paper). Denitration of this ion would lead to the formation of a guanidinium ion and a nitronium ion, a process which requires an additional proton

$$(NH_2)_2C{=}\overset{+}{N}HNO_2 + H^+ \rightleftharpoons (NH_2)_2C{=}\overset{+}{N}H_2 + NO_2^+$$

The proton will be supplied by either of the acid species present, H_3O^+ or H_2SO_4, but bimolecular reaction of either with the nitroguanidinium ion can be excluded, as the previously reported failure[1] of the experimental results to conform to a bimolecular mechanism of this type was confirmed for all compounds now studied. If the additional proton becomes attached to the nitroguanidinium ion in any initial fast step, it will almost certainly be located on one of the two amino-groups and the denitration of the bivalent ion so formed through a transition complex which includes a bisulphate and oxonium ion could be represented as shown



The Brönsted rate equation for this reaction is

$$\text{rate} = k_0\{PH_2^{++}\}\{H_3O^+\}\{HSO_4^-\}/f_\ddagger$$

and the experimental rate $= k[PH^+]$ where PH^+ and PH_2^{++} represent the monoprotonated and diprotonated nitroguanidine respectively, and $f_\ddagger$ is the activity coefficient of the transition complex:

$$k = k_0\{PH_2^{++}\}\{H_3O^+\}\{HSO_4^-\}/[Ph^+]f_\ddagger$$

From the equilibria $H_2O + H_2SO_4 \rightleftharpoons H_3O^+ + HSO_4^-$; $PH^+ + H^+ \rightleftharpoons PH_2^{++}$ which have the thermodynamic equilibrium constants K_{H_2O} and $K_{PH_2^{++}}$, respectively, we have

$$k = k_0K_{PH_2^{++}}K_{H_2O}\{H^+\}\{H_2O\}\{H_2SO_4\}f_{PH^+}/f_\ddagger$$

and since $$H_0 = -\log\{H^+\}f_B/f_{BH^+}$$

$$\log k = \log k_0K_{PH_2^{++}}K_{H_2O} - H_0 + \log\{H_2O\} + \log\{H_2SO_4\} + \log f_{PH^+}\, f_{BH^+}/f_Bf_\ddagger$$

which agrees with the empirical equation 2 if the activity coefficient term remains constant.

The range of media in which this combination of reactant and solvent species could be expected to be formed most readily is from that of the 1 : 1 molar ratio of water to sulphuric acid (84·5%) to that of the 2 : 1 molar ratio (72·5%) since within this range it is probable that H_3O^+ is the strongest proton donator and HSO_4^- the strongest proton acceptor. This range largely coincides with that found experimentally for the application of equation 2.

The aqueous perchloric acid used corresponds in acidity to the aqueous sulphuric acid range below the 2 : 1 molar ratio of water to sulphuric acid. While H_3O^+ is the strongest acid present, there is no base equivalent to the HSO_4^- ion in aqueous perchloric acid and this may be the reason for the slower reaction and the operation of a different mechanism of denitration with the rate depending mainly on the acidity.

Effect of Change of the Initial Concentration of Reactant on the Rate Constant.—The slight decrease in the rate constant of denitration with increase in initial concentration of the nitroguanidine previously[1,3] observed was confirmed for 2-nitrimino-1 : 3-diaza*cyclo*hexane and *NN*-dimethyl-*N'*-nitroguanidine but the effect was dependent on the particular medium in which the rates were measured. In more aqueous media the effect was virtually eliminated. The rate constant for 2-nitrimino-1 : 3-diaza*cyclo*pentane was independent of initial concentration of reactant over a twenty-fold range from $4{\cdot}5 \times 10^{-3}$ to 10^{-1} mole/l.; a similar result was found for the 4-methyl analogue. No conclusion has been reached on this difference in behaviour of nitroguanidines.

The Extent of Denitration at Equilibrium.—Although rates of denitration become immeasurably fast above 90% sulphuric acid for all but one of the compounds in Table 1, data on the equilibria attained in all media up to *ca.* 95% sulphuric acid were obtained by determining the equilibrium concentration of the nitroguanidine spectroscopically. Equilibrium concentrations were also measured for the denitration of the diaza*cyclo*hexane and of *N*-methyl-*N'*-nitroguanidine in perchloric acid and for the same equilibrium attained by guanidine nitrate in sulphuric acid–acetic acid. The variation in the extent of denitration in aqueous sulphuric acid with medium composition is shown in Fig. 2; a minimum for all compounds occurs at 85—88% sulphuric acid. With sulphuric acid–acetic acid there is a similar minimum at 73% sulphuric acid. In both sulphuric acid–water and sulphuric acid–acetic acid, the composition of the media where the minimum occurs is such that the mole ratio of sulphuric acid to the other component is greater than 1 but in the strongest perchloric acid used (72%) this ratio is much less than 1. A minimum is therefore not observed in the latter because a sufficiently high mole ratio of acid to water cannot be attained.

Since the percentage denitration is a measure of the ratio of the rate of denitration to rate of nitration, it is evident that as the acid strength increases, the rate of nitration at first increases more rapidly than that of denitration, but as the point of minimum denitration is approached this difference is not maintained. The rate of denitration increases sharply above this point as the results for 2-nitrimino-1 : 3-diaza*cyclo*pentane (Table 1) indicate; if the nitration shows the same phenomenon of attaining a maximum rate in *ca.* 90% sulphuric acid as already established for aromatic nitration[23] the occurrence of a minimum is to be expected. The corresponding maximum amount of nitration has been found in the equilibria attained in the nitration of tetraethylguanidine in sulphuric acid, the maximum occurring when the water content of the medium is 10—15%.[24]

A relation between the equilibrium constant and the activity of water has been adduced by Simkins and Williams,[2] given by

$$\log K_0 = \log K + \log \{H_2O\} + \log (f_{PH^+}/f_{GH^+}\, f_{HNO_3})$$

where K_0 represents a thermodynamic equilibrium constant, K the ratio of equilibrium concentrations $[PH^+]/[GH^+][HNO_3]$, $\{H_2O\}$ the activity of water, and f_{PH^+}, f_{GH^+}, and f_{HNO_3} the activity coefficient of the nitroguanidine ion, the guanidinium ion, and nitric acid, respectively. This has been tested by plotting log k against log $\{H_2O\}$, for sulphuric acid–water (the only medium for which the necessary data are available). With 2-nitrimino-1 : 3-diaza*cyclo*hexane and *NN*-dimethyl-*N'*-nitroguanidine good straight lines were obtained for media up to that corresponding to minimum denitration with slopes of $-0{\cdot}99$ and $-1{\cdot}23$, respectively. 2-Nitrimino-1 : 3-4-triazole gives an initial

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[23] Bonner, James, Lowen, and Williams, *Nature*, 1949, **163**, 955.

[24] Kirkwood and Wright, *Canad. J. Chem.*, 1957, **35**, 527.

straight-line plot of slope $-0{\cdot}90$, but this falls off rapidly above 80% sulphuric acid. For 2-nitrimino-1 : 3-diaza*cyclo*pentane and its 4-methyl derivative, the extent of denitration is more than 80% in most media, and the back reaction occurs to such a slight extent that it is not possible to deduce reliable values for K.

Rates, k_2, of the nitration can be calculated from the equilibrium constant K and the rate of the forward reaction k, since $K = k_2/k_1$. Reliable values are only possible for 2-nitramino-1 : 3 : 4-triazole, 2-nitrimino-1 : 3-diaza*cyclo*hexane, and *NN*-dimethyl-*N'*-nitroguanidine since the equilibrium is displaced too far in favour of the forward reaction for the other two compounds in Table 1.

Comparison of the rates of nitration for these three compounds with the acidity function J_0 [25] confirms that nitration of guanidines occurs through the nitronium ion; in each case log k_2 is a linear function of J_0 with slope approximately as indicated: 2-amino-1 : 3 : 4-triazole (0·97), 2-imino-1 : 3-diaza*cyclo*hexane (0·83), and *NN'*-dimethylguanidine (0·94).

Some attempt was made to measure the rate of nitration of guanidine in sulphuric acid–acetic acid but although preliminary results suggest 99% conversion of the guanidine, substantial decomposition to products other than nitroguanidine was evident, and further investigation of these side-reactions is necessary.

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[*Received, May 1st*, 1958.]

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