MECHANISM OF GUANIDINE NITRATION

II. TETRAETHYLNITROGUANIDINE[1]

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ABSTRACT

The preparation of *sym*-tetraethylnitroguanidine now shows that a ketimino group can be nitrated directly. The mode of nitration has been evaluated first by determination of the ionization of guanidine bisulphate (prepared anew) and tetraethylguanidine in nearly-anhydrous sulphuric acid by means of an improved cryoscope, and by comparison of these ionizations with those of substances the ionizing behavior of which may be reliably predicted. Subsequent studies show that the stronger base, *sym*-tetraethylguanidine, is nitrated more slowly than guanidine, both reactions being reversible. Detailed kinetic studies were not made because of the irreversible side-reaction yielding tetraethylurea. This irreversible reaction, which is suppressed by sodium bisulphate but not by nitric acid, is presumptive for the existence of an intermediate nitrotetraethylguanidinium salt out of which the tetraethylnitroguanidine or tetraethylurea may arise.

In the first paper of this series (33) it was suggested that nitration of a guanidine occurs at the imino rather than a primary amino nitrogen. In order to test this hypothesis we have examined *sym*-tetraethylguanidine in which only the imino nitrogen is available for replacement of hydrogen by a nitro-group. Nitration does not occur in a nitric acid – acetic anhydride system, but in a nitric acid – sulphuric acid system a 61% yield of *sym*-tetraethylnitroguanidine is obtained. The substance has been characterized by analysis and by alkaline hydrolysis to yield tetraethylurea.

This authentic nitrimine resembles nitroguanidine in many respects. Thus its absorption maximum at 268 mμ is near to that of nitroguanidine (265 mμ), though different from a previous specification of nitrimine absorption (20). The infrared spectra of tetraethylnitroguanidine and nitroguanidine are not comparable because the principal absorption (6.8–7.0 μ) found for the new compound as a supercooled liquid is masked by the mineral oil used for the mull of nitroguanidine (16). However both substances behave similarly by negative Franchimont tests for the nitramine linkage (9). Finally the electric moment of 7.64 D., determined in dioxane at 20°, is higher than that of nitroguanidine (μ = 6.95 D.) (15) by about the contribution that would be expected from the effect of four ethyl groups tetrahedrally disposed at the amino nitrogens. These similarities tend to confirm the nitrimino structure which has been proposed for nitroguanidine (1).

Thus the nitration of tetraethylguanidine seems to resemble that of guanidine, but the rate of nitration is slower. Insofar as imine nitration is thought to resemble secondary amine nitration this result would not be unexpected if tetraethylguanidine were more strongly basic than guanidine (8). Since direct evaluation of electron-donation is of questionable significance in strong sulphuric acid, we have examined instead the extent of salt dissociation by cryoscopic means.

For this cryoscopic evaluation we have prepared the hitherto-unknown guanidine bisulphate, an easily purified anhydrous salt. A salt of tetraethylguanidine satisfactory for cryoscopic study could not be found so the carbonate-free amine was used for the purpose. We have included comparative studies with benzoic acid, trinitrotoluene, dimethylsulphone, and *p*-tolyltrimethylammonium bisulphate. Surprisingly we have

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found the latter salt to be satisfactory for cryoscopic studies although Williams and his co-workers (18) reported unworkable hygroscopicity. Possibly they encountered the sulphate salt.

In common with other workers (10, 12) we have found that freezing point determinations in absolute sulphuric acid lead to i values ($\Delta°$ found/$\Delta°$ calc. from molecular weight of solute) which depend on the amount of solute present. Typical is the behavior of benzoic acid, the first item in Table I, using Gillespie's cryoscopic constant (5.98°/g. mole^{-1}. kg.) for absolute sulphuric acid. The freezing point depressions in the first two determinations are smaller than would be expected if benzoic acid dissociates in absolute sulphuric acid according to equation (i):

$$C_6H_5COOH + H_2SO_4 \rightleftarrows C_6H_5CO_2H_2^{\oplus} + HSO_4^{\ominus} \qquad \text{(i)}$$

but the expected result according to equation (i) is obtained (determination 3) when the concentration of solute is increased further.

This behavior has been explained (10, 12) as due to alteration, by the bisulphate ion generated according to equation (i), of the autoprotolysis of sulphuric acid

$$2H_2SO_4 \rightleftarrows H_3SO_4^{\oplus} + HSO_4^{\ominus} \qquad \text{(ii)}$$

ince a shift of (ii) to the left would reduce the particle concentration. According to this explanation the mass effect should decrease with increasing amounts of solute.

The validity of this argument may be questioned, and indeed it has been shown that indiscriminate addition of bisulphate salts leads to ambiguous results (5). Actually the i values for benzoic acid are consistent over a series of concentrations of solute (determinations 4–9 inclusive) when the sulphuric acid is 0.03 molar in water. But this inclusion, which has been thought to contribute sufficient hydronium bisulphate to compensate reaction (ii), causes an apparent dissociation which exceeds that expected of reaction (i). This discrepancy has been evaluated by examination of other substances the dissociations of which are thought to be known.

It has been demonstrated spectroscopically (4) that trinitrotoluene does not react with anhydrous sulphuric acid. We have examined this substance in anhydrous sulphuric acid as well as that containing 0.03 mole per liter of water (determinations 10–21 inclusive, Table I) and find that the i values are essentially the same in both media although they are higher than the expected value of unity. This discrepancy may be due to the use of Gillespie's freezing point constant in a system to which it is not applicable.

A further test of this constant has been made by study of dimethysulphone upon the assumption that it does not undergo salt formation in absolute, or nearly-absolute, sulphuric acid. However the determinations (22–27 inclusive, Table I) do not confirm this assumption. It may be seen that increasing concentration of solute in absolute sulphuric acid causes increasing i values, the maximum of which is about the same as that observed for all solute concentration in sulphuric acid 0.03 molar in water. This might be considered as evidence of partial ionization in the systems.

It was hoped that an examination of trimethyl-p-tolylammonium bisulphate would specify the freezing point constant since this quaternary ammonium salt might be expected to be so completely dissociated in sulphuric acid that the system would be characterized by an i value of 2. This hope has not been realized. Determinations 28–30 inclusive (Table I) show increasing i values with increasing concentration despite the use of a sulphuric acid which is not anhydrous. Furthermore the maximum i value,

TABLE I

DEPRESSIONS OF THE FREEZING POINT OF SULPHURIC ACID CAUSED BY SUCCESSIVE ADDITIONS OF SOLUTE

Solute			Sulphuric acid				
Name	Wt., g.	F.P. No.	Wt., g.	Molal content of water	Δ° C. found	Δ° C. calc.	"*i*" value
Benzoic acid	.0471	1	29.30	Nil	.140	.078	1.74
	.0872	2	,,	Nil	.269	.145	1.85
	.1295	3	,,	Nil	.433	.216	2.00
	.0361	4	28.66	.03	.140	.062	2.26
	.0968	5	,,	.03	.352	.166	2.12
	.1345	6	,,	.03	.482	.230	2.10
	.0315	7	31.30	.03	.103	.049	2.11
	.0802	8	,,	.03	.272	.216	2.16
	.1472	9	,,	.03	.482	.231	2.09
Trinitrotoluene	.0371	10	29.67	Nil	.079	.065	1.21
	.1586	11	,,	Nil	.164	.141	1.16
	.2331	12	,,	Nil	.233	.207	1.13
	.0633	13	33.22	Nil	.057	.050	1.14
	.1417	14	,,	Nil	.129	.112	1.15
	.2230	15	,,	Nil	.206	.178	1.16
	.0671	16	31.07	.02	.065	.057	1.14
	.1298	17	,,	.02	.124	.110	1.13
	.2090	18	,,	.02	.209	.178	1.17
	.0582	19	34.26	.03	.053	.045	1.17
	.1187	20	,,	.03	.105	.091	1.15
	.1930	21	,,	.03	.171	.149	1.15
Dimethylsulphone	.0278	22	29.77	Nil	.065	.060	1.03
	.0610	23	,,	Nil	.147	.131	1.12
	.1072	24	,,	Nil	.271	.229	1.18
	.0361	25	31.89	.03	.084	.072	1.17
	.0717	26	,,	.03	.168	.143	1.18
	.1050	27	,,	.03	.251	.210	1.19
Trimethyl-*p*-tolyl-ammonium bisulphate	.0923	28	30.09	.03	.142	.074	1.92
	.1462	29	,,	.03	.234	.118	1.98
	.2354	30	,,	.03	.403	.189	2.13
Guanidine bisulphate	.0892	31	31.41	Nil	.136	.108	1.26
	.1714	32	,,	Nil	.352	.208	1.69
	.2380	33	,,	Nil	.550	.288	1.91
	.3225	34	,,	Nil	.799	.391	2.04
	.0841	35	29.51	.03	.265	.109	2.43
	.1706	36	,,	.03	.528	.220	2.40
	.2219	37	,,	.03	.704	.286	2.46
	.3078	38	,,	.03	.966	.396	2.44
sym-Tetraethylguanidine	.0416	39	29.72	.03	.149	.049	3.04
	.0902	40	,,	.03	.316	.107	2.95
	.1378	41	,,	.03	.497	.162	3.07
	.0355	42	34.37	.03	.117	.036	3.24
	.0742	43	,,	.03	.229	.076	3.02
	.1230	44	,,	.03	.367	.126	2.92

2.13, exceeds the theoretical value of 2 by approximately the same discrepancy that has been observed for the three other test substances which were examined. This (so-called) discrepancy cannot be a function of time, at least for determination 30, Table I, because the difference (10.308° − 9.905°) was reproducible within 0.001° 12 hours after the original measurement.

In view of these results we are inclined to agree with Wyatt (34), and indeed to extend his opinion to electrolytes, that the cryoscopic method is inaccurate as an evaluation

of basic strength. Nevertheless comparison with the same type of substance ought to be qualitatively valid, and this we have done with guanidine and tetraethylguanidine.

Upon the basis of freezing point lowering caused by guanidine carbonate in absolute sulphuric acid Hantzsch and Geidel (13) considered this amidine to be triprotonated. However, decomposition of the carbonate added an equivalent of water so that the medium was about 0.03 molar in water. Recalculation of Hantzsch's data with use of Gillespie's cryoscopic constant reduces the i value to about 2.8.

Other workers (31) have studied the behavior of the benzoate, perchlorate, and benzenesulphonate of guanidine in sulphuric acid about 0.03 molar in water and have arrived at an i value of about 2.4. It may be seen (determinations 35–38 inclusive, Table I) that our values obtained from guanidine bisulphate in nearly-anhydrous sulphuric acid are in agreement. In absolute sulphuric acid we observe the same i value increase with increasing concentration which is characteristic of the other solutes that we and others have examined.

TABLE II

INTERCONVERSION OF *sym*-TETRAETHYLGUANIDINE (STEG) AND TETRAETHYLNITROGUANIDINE (STENG) IN SULPHURIC ACID SUBSTRATE AT 0°

Expt.	Wt.% H_2O in substrate	Mole ratio $\frac{HNO_3}{STEG}$	Time, hr.	Analyses, mole/l. STEG	Analyses, mole/l. STENG	% STEG accounted for
1	5	5.06	0	.341	0	—
			0.25	.205	.120	95
			0.75	.141	.175	93
			1.0	.119	.192	91
			1.5	.091	.216	90
			2.0	.067	.235	89
			5.0	.020	.274	86
			10.0	.012	.265	81
			24.0	.012	.231	71
2	5	1.14	0	.353	0	—
			0.5	.329	.019	99
			1.5	.370	.029	95
			3.5	.288	.044	94
			6.5	.266	.062	93
			11.5	.256	.074	92
			26.5	.234	.080	89
3	8.8	5.86	0	.290	0	—
			0.16	.164	.119	98
			0.40	.118	.147	91
			0.66	.097	.170	92
			1.16	.058	.200	89
			2.00	.031	.232	91
			4.00	.0082	.246	88
			6.0	.0045	.246	86
			8.0	.0046	.242	85
			20.0	.0044	.209	73
4	8.8	1.35	0	.311	0	—
			0.33	.263	.035	96
			1.33	.223	.064	92
			5.00	.156	.129	92
			10.0	.089	.183	87
			23.0	.052	.210	84
5	16.2	5.18	0	.361	0	—
			0.16	.323	.020	95
			0.50	.295	.038	92
			1.5	.245	.089	93

TABLE II—*concluded*

INTERCONVERSION OF *sym*-TETRAETHYLGUANIDINE (STEG) AND TETRAETHYLNITROGUANIDINE (STENG) IN SULPHURIC ACID SUBSTRATE AT 0°

Expt.	Wt.% H_2O in substrate	Mole ratio $\frac{HNO_3}{STEG}$	Time, hr.	Analyses, mole/l. STEG	Analyses, mole/l. STENG	% STEG accounted for
			3.5	.165	.157	89
			5.5	.118	.208	90
			8.5	.071	.246	88
			23.5	.015	.299	87
			33.5	.009	.300	86
6	16.2	1.45	0	.340	0	—
			2.25	.286	.030	93
			8.25	.222	.088	91
			25.2	.126	.163	85
			35.3	.091	.171	77
7	5		0	0	.244	—
			0.25	.017	.208	92
			0.4	.026	.197	91
			0.66	.025	.190	88
			1.0	.038	.181	90
			2.16	.059	.155	88
			4.25	.095	.116	86
			7.0	.101	.082	75
			24.0	.144	.024	69
			53.0	.145	.019	67
8	8.8	∞	0	0	.171	—
			0.5	.004	.151	91
			2.0	.006	.147	90
			5.0	.012	.135	87
			10.0	.020	.124	84
			21.5	.033	.094	74
			34.0	.035	.081	68
			46.0	.038	.075	66
9	16.2	∞	0	0	1.70	—
			0.5	0	1.56	91
			1.0	0	1.58	93
			2.0	0	1.56	91
			4.0	0	1.56	91
			8.0	.0007	1.55	91
			25.0	.0030	1.52	91
			54.0	.0051	1.48	90
10	8.8	Footnote A	0	0	.170	—
			0.5	.0017	.158	94
			2.0	.0021	.151	90
			4.5	.0025	.145	87
			9.5	.0025	.137	82
			21.0	.0021	.129	77
			34.0	.0019	.117	70
			46.0	.0020	.101	61
11	8.8	Footnote B	0	0	.170	—
			0.5	.0071	.147	91
			1.5	.0117	.142	91
			4.5	.0301	.120	88
			9.5	.0453	.103	87
			24.0	.0666	.079	86
			34.0	.0748	.062	81
			53.0	.0794	.055	79

(*A*) *Nitric acid added to give mole ratio of HNO_3/STENG equal to 5.25.*
(*B*) *Sodium bisulphate added to give mole ratio of $NaHSO_4$/STENG equal to 4.20.*

We would have preferred to examine *sym*-tetraethylguanidine exactly like guanidine but we were unable to prepare a sulphate salt of the tetraethyl homologue which was sufficiently non-hygroscopic for freezing point determination. However the base itself was amenable to use in nearly-anhydrous sulphuric acid. As Table I (determinations 39–44 inclusive) shows, the compound is a stronger proton acceptor than guanidine in sulphuric acid, in conformity with its lesser rate of nitration.

Similarly with guanidine (28, 32) the nitration of tetraethylguanidine is reversible. Solutions of 0.09 g. of the nitro compound in 1 g. of 96.6% and 95.0% sulphuric acids after 60 minutes gave precipitates of nitron nitrate equivalent to 12.6% and 1.7% of denitration respectively. On the other hand no nitron nitrate could be detected after 60 minutes in 92.8% sulphuric acid. The denitration is thus critically dependent on the alteration of the system by water.

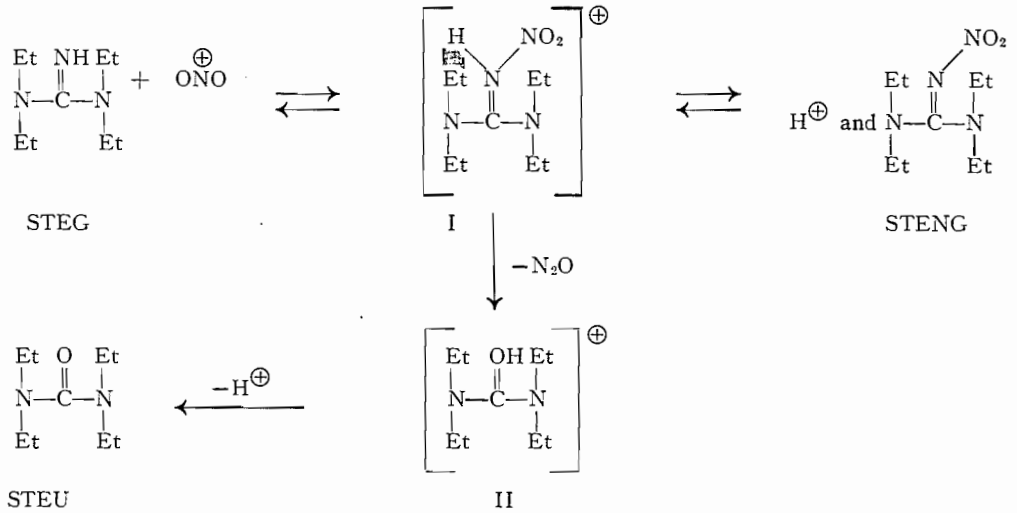
A detailed study of the nitration of *sym*-tetraethylguanidine (STEG) and the denitration of *sym*-tetraethylnitroguanidine (STENG) has been accomplished by separation of STEG and STENG from the reaction system by means of ion-exchange resins with subsequent evaluation of each by ultraviolet absorption intensities. Comparative reactions have been carried out in 95%, 91.2%, and 83.8% sulphuric acid.

The data of Expts. 2, 4, and 6, Table II, in which a ratio of nitric acid to STEG slightly greater than 1 is maintained, show that the maximum reaction rate occurs when the water content of the medium is about 10–15%. This phenomenon has been observed in the nitration of amides (27), amidines like guanidine (26), and aromatic nitro-compounds (19, 3, 30). Since the rate maximum is approximately the same for nitration of these several types it is evident that the behavior is principally a function of the properties of the sulphuric acid medium. An adequate explanation, which has not yet been forthcoming, must await a new insight into the nature of this common, yet little-understood, substance called sulphuric acid.

Inspection of Expts. 1 and 3 (less apparent, 5) shows that the yield of tetraethylnitroguanidine (STENG) with respect to time is only temporarily maximal. This evidence of a side reaction, indicated also by the per cent of tetraethylguanidine (STEG) not accounted for by the analytical method, has been confirmed by examination of a system in 95% sulphuric acid which was allowed to proceed to completion. The identification of tetraethylurea and nitrous oxide shows that this side reaction is an irreversible decomposition of the desired product, STENG, and the kinetic data show that this decomposition is faster in stronger sulphuric acid.

This irreversible decomposition has been confirmed by treatment of the desired nitration product, STENG, with aqueous sulphuric acid containing 95, 91.2, and 83.8% of the acid. Experiments 7, 8, and 9 show that the rapid reversible denitration reaction is followed by a slower irreversible reaction which must be the decomposition of *sym*-tetraethylnitroguanidine (STENG) to tetraethylurea and nitrous oxide. It is shown (Expt. 10) that this irreversible decomposition is not affected appreciably by excess of nitric acid, although, as might be expected, the nitric acid represses the reversible denitration. On the other hand it is of interest to note that the addition of sodium bisulphite (Expt. 11) has little effect on the reversible denitration but it retards profoundly the irreversible decomposition in which tetraethylguanidine disappears from the system.

Assuming that this bisulphate salt operates by protonic capture, one may formulate the following reaction series to explain these phenomena:



According to this concept, nitration proceeds by coordination of nitronium ion with STEG to give the ammononitronium ion I. This ion may be converted reversibly to either STEG, the tetraethylguanidine, or else the nitration product STENG with loss of a proton. An excess of nitric acid forces the equilibrium from STEG to STENG without decreasing the concentration of the intermediate ion I whereas sodium bisulphate, by inactivation of both nitronium and hydrogen ion (or its solvated equivalent), reduces the concentration of I. But the complex ion I may also decompose irreversibly by loss of nitrous oxide to yield ephemerally the tetraethylisourea cation II which, by loss of hydrogen ion or its equivalent, appears as *sym*-tetraethylurea, STEU.

Such a concept has been shown to be untenable in the instance of, say, toluene nitration (21, 2), where the absence of an isotope effect precludes an equilibrium between complex nitronium ion and product, which would be shifted by presence of bisulphate ion. However the difference in coordinative power between toluene and tetraethylguanidine is profound, and a significant concentration of ammononitronium ion I is not unexpected. In the present instance it is of interest to examine a nitratable compound, the cation acceptance of which is intermediate between STEG and toluene.

The nitration of guanidine, which falls into this category, has been studied by Williams and Simkins (32). There is no detectable tendency in this reaction to form the urea as a by-product, at least at the lowest temperature (15°) which these workers employed. In order to establish a basis for comparison with tetraethylguanidine we have nitrated guanidine (as the carbonate) at 0° in sulphuric acid initially containing 16.2% of water (see Table III). We find that the reaction is almost complete within 5 minutes, and no decomposition of the product occurs. Comparison of this nitration rate with that of tetraethylnitroguanidine under the same conditions (Table II) shows that nitroguanidine is formed about 700 times as fast as its tetraethyl homologue. Since the nucleophilicity

TABLE III

NITRATION OF GUANIDINE IN 83.8% SULPHURIC ACID AT 0°
Initial moles guanidine carbonate: moles HNO_3 = 0.411 mole/liter: 0.569 = 1.38

Time, min.	5	20	60	240	600
Conc. nitroguanidine, moles/l.	0.378	0.389	0.401	0.378	0.389

of guanidine is less than that of tetraethylguanidine (STEG, Table I) it would seem that the nitration rate was dependent on a balance between acquirement of alternative ions, exemplified in the formulation above as nitronium and hydrogen ions. Essentially this is the behavior of secondary amines with respect to nitration, thus justifying a formal relationship between R_2NH and R_2CNH (6, 8).

We believe that the general tendency of the nitroguanidines toward decomposition into nitrous oxide and the analogous ureas also supports the concept of the intermediacy of complex nitronium salts during nitration of amines. Although nitroguanidine itself does not undergo this decomposition in the acid reaction media at 25° (32) it is unstable in this respect at higher temperatures (14). This decomposition might have occurred via a primary nitramino group in nitroguanidine but this path obviously is impossible for *sym*-tetraethylnitroguanidine. Insofar as the two guanidines are analogous the nitration may be considered to operate through a complex cation such as I, which ought to behave toward excess nitric acid and toward sodium bisulphate in the manner which we observed during nitration of STEG.

EXPERIMENTAL*

sym-Tetraethylnitroguanidine, STENG

To a solution of 1.71 g. (0.01 mole) of *sym*-tetraethylguanidine (24, the final Grignard reaction should stand for 10 hours prior to hydrolysis) in 14.7 g. (0.15 mole) of 100% sulphuric acid at 0° C. was added with stirring over a period of 20 minutes, 3.15 g. (0.05 mole) of 99.9% nitric acid. The colorless reaction system was maintained at 0° C. for 60 minutes and then was dripped slowly onto 25 g. of crushed ice. The drowned reaction system was then neutralized by addition of solid sodium carbonate and the amber oil which separated was collected by three 25-ml. extractions with chloroform. The combined extract, dried by magnesium sulphate, was distilled, first at 25° C. (20 mm., 1.65 g.), and then at 0.01 mm., to yield 0.01 g., b.p. 55° C. (identified as tetraethylurea by conversion to its chloroplatinate), and then 1.33 g. (61%), b.p. 141–142° C., solid at 30° C. Low temperature crystallization from ethyl acetate gave a melting point of 37.3–38.0° C. Calc. for $C_9H_{20}O_2N_4$: C, 50.0; H, 9.32; N, 25.9. Found: C, 49.8; H, 9.07; N, 26.0. The substance showed an absorption band at 268 mμ (molar extinction coefficient, 1.195×10^4) as contrasted to tetraethylguanidine with a band at 227 mμ where the nitro compound again absorbed strongly. The infrared spectrum is recorded in μ at K_e, 2.95 [0.921], 3.35 [6.12], 3.45 [6.10], 6.50 [1.171], 6.68 [0.968], 6.85 [1.302], 6.95 [1.378], 7.25 [0.798], 7.48 [0.635], 7.67 [0.783], 7.80 [0.916], 8.05 [2.931], 8.75 [0.744], 8.90 [0.724], 9.05 [0.761], 9.26 [0.798], 9.85 [0.607], 10.10 [0.654], 10.50 [0.519], 10.60 [0.548], 10.75 [0.611], 12.10 [0.394], 12.45 [0.494], 12.65 [0.536], 12.85 [0.494], 13.40 [0.616], 13.50 [0.629]. The electric moment in dioxane at 500 kc. at 200° C. is 7.64 D., calculated by the method of Halverstadt and Kumler (11); P (total) = 1290 cc.; MR_D calc.: 61.1 cc., found from n_D^{20} 1.51880 and d_4^{20} 1.037 using supercooled liquid: 63.2. However, if the atomic polarization determined for nitroguanidine from the dielectric constant of solid pellets (22) at maximum density ($P_a = P_{e+a} - MR_D = 30.4 - 23.2 = 7.2$ cc.) applies to the tetraethyl analogue, then μ for STENG = 7.61 D. STENG does not give a true Franchimont test for secondary nitramines although a green color develops on the zinc surface in diethylaniline – acetic acid. The X-ray diffraction pattern, determined with Cu K_α radiation (Ni filtered), is reported as intensities [I/I_1] at spacings

Melting points have been corrected against reliable standards (Can. J. Technol. **34, 89 (1956)).*

in Ångstroms: [10] 4.84; [9] 8.11; [7] 3.95; [6] 7.02, 3.80; [5] 8.75, 5.50, 3.56, 3.50; [4] 5.77, 3.18, 2.92; [2] 2.62, 2.49; [1] 4.36, 4.10, 3.03, 2.39.

Tetraethylurea

a. By Decomposition of Tetraethylnitroguanidine in Alkali

A mixture of 0.50 g. (0.0025 mole) of tetraethylnitroguanidine and 5 ml. of 20% aqueous sodium hydroxide (0.025 mole) was heated under reflux for 150 minutes. The cooled two-phase system was twice extracted with chloroform and the 20 ml. of extract, dried with magnesium sulphate, was vacuum-evaporated. The residue (0.31 g.) was distilled, b.p. 90–91° C. (9 mm.), 0.16 g. (40%); the chloroplatinate did not depress the melting point of an authentic sample.

b. By Decomposition in 96% Sulphuric Acid

A mixture of 0.669 g. (0.0031 mole) of tetraethylnitroguanidine and 5 ml. of 96% sulphuric acid was stirred magnetically at 20° C. for 1 day while the evolved gas was collected over water. By combustion with hydrogen this gas was found to contain 18.4 cc. of nitrous oxide (27%). The remaining liquid was poured onto ice and diluted to 100 ml. with water. Threefold extraction with ether followed by processing as described above gave a 51% yield of authentic tetraethylurea.

c. From Diethylamine and Phosgene

This product, prepared by the method of Michler (23), did not give the chloroplatinate (m.p. 134° C. but not analyzed) reported previously (25) but instead a chloroplatinate with m.p. 98–99° C. Calc. for $(C_9H_{20}N_2O)_2H_2PtCl_6$: Pt, 25.9. Found: Pt, 26.6.

Guanidine Bisulphate

To 13 ml. (0.25 mole) of 100% sulphuric acid in a flask protected from air was added in small quantities 15.1 g. (0.08 mole) of guanidine carbonate. Upon cooling to 20° C. the system became a white slush which was triturated seven times with 100-ml. volumes of diethyl ether in order to remove the excess sulphuric acid. Subsequently the ether-insoluble portion was filtered off and dried to constant weight *in vacuo*, 23.6 g. (89%), m.p. 101.0–101.5° C. after two crystallizations from hot acetic acid. Calc. for $CH_7O_4N_3S$: N, 26.7; SO_4, 61.1. Found: N, 26.2; SO_4, 60.9. The picrate prepared from this salt melted at 325–330° C.; admixture with authentic guanidine picrate did not depress this melting point.

p-Tolyltrimethylammonium Bisulphate

A solution of 15.0 g. (0.054 mole) of *p*-tolyltrimethylammonium iodide (prepared from *p*-dimethyltoluidine and methyl iodide in anhydrous diethyl ether) in 200 ml. of 95% ethanol was treated with small quantities of freshly-precipitated silver oxide until the formation of silver iodide was no longer evident. The silver salts were then filtered off and washed well with 95% ethanol. Filtrate and washings, combined, were chilled to 0° C. Then 96% sulphuric acid was added slowly until the pH of the system reached about 2. After vacuum evaporation of the solvent the amber gummy solid was redissolved in 125 ml. of absolute ethanol and this solution was decolorized by Norit. Subsequent addition of 150–200 ml. of absolute diethyl ether gave 9.61 g. (72%) of white leaflets, m.p. 133–136° C. This crude bisulphate was purified by solution in absolute ethanol followed by precipitation with absolute ether, m.p. 132.5–133.3° C. Calc. for $C_{10}H_{17}O_4NS$:

SO_4, 38.9. Found: SO_4, 38.9. The melting point of the picrate prepared from this salt (m.p. 197–198° C.) was not depressed by admixture with an authentic sample (29).

Dimethyl Sulphone

This substance, prepared by hydrogen peroxide oxidation of dimethyl sulphide (7), was dissolved in 80 ml. of saturated aqueous sodium sulphate and this solution was continuously extracted with chloroform. The extract, dried over sodium sulphate, was vacuum-evaporated and the 3.1 g. (47%), m.p. 107–110° C., was twice crystallized from hot chloroform (10 ml. per g.), m.p. 109.3–110.0° C. (soft 108.5° C.). The literature reports a melting point of 109° C. (17).

Analytical Procedure for Kinetic Studies

In order to separate tetraethylguanidine and tetraethylnitroguanidine from nitric and sulphuric acids, and from each other, the drowned aliquots were passed through a 15×2 cm. column containing Amberlite IR-4-B ion exchange resin (Dowex-2 was too basic and destroyed the nitration product) to retain as much of the mineral acids as possible. Thence the eluate was passed through a column 2 cm. by 0.8 cm. containing Dowex-50 in order to remove tetraethylguanidine. Since this base is stronger than the IR-4-B resin, the eluate from the Dowex-50 contained some sulphuric acid which was subsequently removed by a third column, 5 cm. by 1.5 cm., containing IR-4-B.

The eluate from the three tandem columns contained only tetraethylnitroguanidine. The amount was ascertained by comparison of the absorption spectrum with those of standard solutions via identical columns (see Table IV).

TABLE IV

DETERMINATION OF MOLAR EXTINCTION COEFFICIENT AT 268 mμ OF *sym*-TETRAETHYLNITROGUANIDINE IN AQUEOUS SOLUTION

Conc., mole/l. × 10^{-5}	1.027	2.054	3.081	4.108	5.135	6.162	7.189
Molar extinction coefficient × 10^4	1.199	1.207	1.198	1.184	1.197	1.188	1.213

The tetraethylguanidine was recovered by inverting the Dowex-50 column and washing it with 4 *N* sulphuric acid. The eluted salt in aqueous acid was evaluated by comparison of the absorption spectrum with those of standardized solutions via identical columns (see Table V).

TABLE V

DETERMINATION OF MOLAR EXTINCTION COEFFICIENT AT 227 mμ OF *sym*-TETRAETHYLGUANIDINE IN 4 *N* SULPHURIC ACID

Conc., mole/l. × 10^{-5}	1.43	2.86	4.29	5.72
Molar extinction coefficient × 10^3	9.16	9.19	9.12	9.13

Mixtures of known composition comprising the two compounds were found to be 96–100% recoverable according to spectroscopic analysis, while the presence of tetraethylurea interfered neither with the separation nor with the subsequent spectrometry since the urea is transparent in the spectral regions involved in the analysis.

Kinetic Procedure

The nitration of *sym*-tetraethylguanidine in sulphuric acid, and the subsequent analyses, were carried out as follows. A weighed quantity of tetraethylguanidine was added to the appropriate medium containing sulphuric acid. A solution of absolute

nitric acid in sulphuric acid of the same strength was prepared at 0° C. and the two solutions were mixed at 0° C. and made up rapidly to a volume of 10 ml. by addition of more of the sulphuric acid medium, then shaken rapidly at 0° C. for 1 minute and thereafter maintained at this temperature. Periodically 1-ml. samples were withdrawn and drowned on 20–25 g. of ice. These aliquots were made up to 100-ml. volumes with distilled water and then were passed successively through the ion-exchange columns. Subsequently the three tandem columns were washed with 350 ml. of water. The combined eluates were made up to a 500-ml. volume with distilled water and then diluted appropriately (usually 2 ml. to 25 ml.) for optical density determination at 268 mμ to indicate the amount of tetraethylnitroguanidine.

The Dowex-50 columns were inverted and eluted with 250 ml. of 4 *N* sulphuric acid. The eluates, made up to 300 ml. with the same acid and usually diluted (2 ml. to 25 ml.), also with 4 *N* sulphuric acid, were examined for optical density at 227 mμ for the amount of tetraethylguanidine.

Nitration of Guanidine

A solution of guanidine carbonate in sulphuric acid of known concentration was prepared at 0° C. To this solution was added a solution of 99.9% nitric acid in sulphuric acid of the same known concentration and the whole at 0° C. was made up quickly to 10 ml. with this sulphuric acid. Periodically 1-ml. aliquots were drowned on 20–25 g. of ice, then diluted to about 100 ml. with distilled water and passed through a 15×2 cm. column of Amberlite IR-4-B resin. This column was washed with water until the combined eluates equalled 500 ml., of which 2 ml. diluted to 25 ml. was usually used for optical density measurement at 264 mμ, where guanidine is transparent. The molar extinction coefficient of nitroguanidine at this wavelength was determined with solutions of concentration 5.30, 2.65, and 7.95×10^{-5} mole/liter as 1.56, 1.54, 1.55×10^{4}, or an average of 1.55×10^{4}. Similar solutions of known concentration were passed through the IR-4-B columns to prove by optical density measurement that recoveries of 98.7–99.6% were effected.

Cryoscopy in Sulphuric Acid

A. The Cryostat

In the apparatus shown in Fig. 1 the stainless-steel stirrer is driven by a cam which is rotated by a variable-speed motor. The temperature is measured by means of a Western Electric Type 14-A thermistor (*R* at 0° C. 3.5×10^{5} ohms, at 50° C. 3.5×10^{4} ohms), which is a part of the Wheatstone bridge shown in Fig. 2. Calibration with respect to a U.S. Bureau of Standards thermometer by plotting the logarithm of resistance of the variable arm of the bridge against the reciprocal of absolute temperature at the thermistor shows that the variation is linear and sensitive to 0.001° C.

For operation, the Wheatstone bridge is balanced at approximately 9° C. by adjustment of the variable resistance arm with respect to the galvanometer and then is switched to the Leeds and Northrup Speedomax recorder, the chart paper width of which covers a temperature range of about 0.35° C., thus facilitating readings to at least 0.001° C. In order to cover the range 9.0–10.4° C. four range settings are necessary, and these are available by means of the variable resistance arm of the bridge, which is adjusted to return the recorder pen to the origin at each step. In practice the recorder is connected when a deflection on the table galvanometer shows that solidification is commencing.

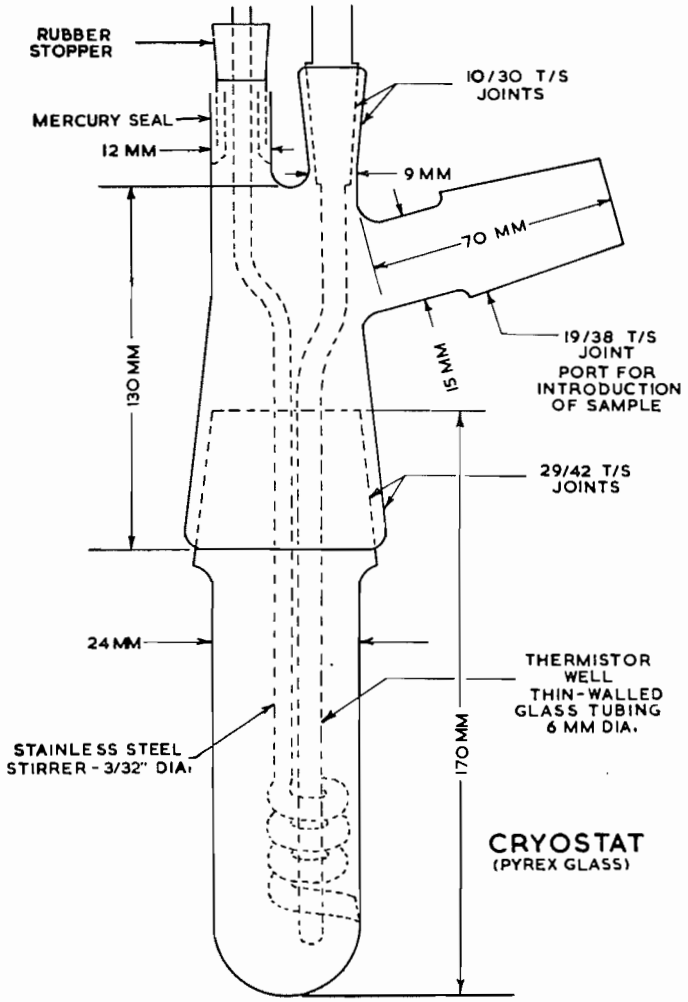


FIG. 1.

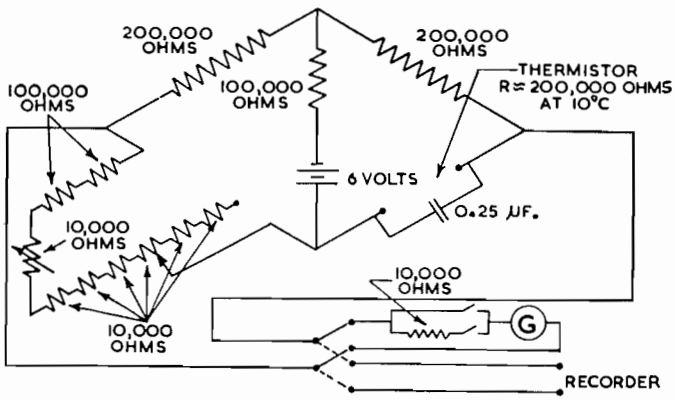


FIG. 2. Electrical circuit for measuring temperature changes in cryostat No. 2.

B. Procedure

Between 25 and 35 g. of absolute sulphuric acid is pipetted into the lower extremity of the cryostat, which previously has been flamed during passage of dry nitrogen through it. An air jacket with an inlet tube is then fitted around the lower extremity of the cryostat and the assembly is immersed in a bath of crushed ice. The sulphuric acid is then stirred under a slight positive pressure of nitrogen at the rate of 90 to 95 strokes per minute of the stainless-steel stirrer (Fig. 1). It is essential to the success of the experiment that the lowest extremity of the stirrer scrapes the wall of the cryostat during the entire stroke.

When the temperature of the sulphuric acid is about 2° C. above the freezing point a piece of dry ice (2 cm. by 0.5 cm. by 0.5 cm.) is passed along the lateral inlet tube of the air jacket and is pressed against the wall of the cryostat for 45 seconds. The seeds of sulphuric acid which form on the interior wall are dispersed through the medium by the action of the stirrer as it scrapes along the wall of the cryostat. In this manner supercooling of anhydrous sulphuric acid is avoided entirely and a time–temperature cooling curve is obtained without the necessity for corrections (10).

The solute, weighed into a very-thin-walled glass tube, is introduced into the cryostat through the 19/38 joint (Fig. 1) and is crushed manually against the wall of the cryostat with the aid of the stirrer in order to ensure uniform distribution throughout the cryoscopic medium. The freezing point is then determined from the chart record by reference to the calibration curve for the thermistor used in the bridge circuit. The results are reproducible to at least 0.003° C. if, and only if, current has been passed through the thermistor for about 12 hours prior to the determination.

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