

Table IV. Limiting Activity Coefficients and Azeotropic Data

| | Margules Constants | | Azeotropic Data | |
|--------------|--------------------|-------|-----------------|---------|
| | MA | MB | x_1 | t_a^a |
| Methanol-EA | | | | |
| Murti (5) | | | 0.705 | 62.4 |
| Nagata (6) | 0.43 | 0.45 | 0.712 | 62.4 |
| Akita (1) | 0.430 | 0.430 | 0.710 | 62.3 |
| This work | 0.45 | 0.43 | 0.715 | 62.2 |
| Methanol-IPE | | | | |
| This work | 0.56 | 0.62 | 0.530 | 57.0 |

^a Boiling temperature of azeotrope, ° C.

is always less than 1200 mm. of Hg in the temperature range studied. At these conditions, the correction factor due to the vapor phase imperfection was negligible. As the t - x - y diagram in Figures 1 and 2 illustrates, the maximum boiling azeotrope in methanol-EA system occurs at 62.2° C. and consists of 71.5 mole % of methanol. Methanol-IPE is also shown to form an azeotropic mixture at 57.0° C. where mole % of methanol is 53.0.

The Redlich-Kister thermodynamic consistency test (9), modified by Herington (2) for isobaric data, showed that the present data are thermodynamically consistent.

The data can well be correlated with the 2-constant Margules equation:

$$\left. \begin{aligned} \log \gamma_1 &= x_2^2 [MA + 2(MB - MA)x_1] \\ \log \gamma_2 &= x_1^2 [MB + 2(MA - MB)x_2] \end{aligned} \right\} \quad (2)$$

where the subscript 1 refers to methanol. A set of the Margules constants were evaluated from the data and tabulated in Table IV, and the experimental and calculated γ values are plotted in Figure 3.

The vapor-liquid equilibrium data for methanol-EA system were reported by Murti (5), Nagata (6), and Akita

(1) and are also incorporated in Figure 1. This comparison shows that the four independent measurements agree with each other, and the still used in this study produces consistent data. A comparison of azeotropic data is also given in Table IV.

NOMENCLATURE

- MA, MB = Margules constants
 p = vapor pressure of pure liquid, mm. Hg
 t = boiling temperature, ° C.
 x, y = composition of liquid and vapor mole fraction, respectively
 γ = activity coefficient
 π = total pressure, mm. Hg

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Properties of 1,1,3,3-Tetramethylguanidine as a Nonaqueous Solvent

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A number of physical constants of 1,1,3,3-tetramethylguanidine (TMG) have been determined and indicate self-association in the liquid presumably through hydrogen bonding. The solvent has a dielectric constant of 11.5. Solubilities of alkali metal salts parallel those in liquid ammonia, but TMG has somewhat weaker dissolving power. In the presence of water, TMG is hydrolyzed to 1,1-dimethylurea; moist TMG reacts with carbon dioxide to form tetramethylguanidinium bicarbonate. The solvent titrates as a strong monoprotic base in aqueous or nonaqueous media. Infrared spectra give evidence for protonation of TMG at the imine nitrogen.

THIS investigation was undertaken to evaluate 1,1,3,3-tetramethylguanidine, $(H_3C)_2NC(:NH)N(CH_3)_2$, as a solvent for inorganic reactions. Recently Longhi and Drago (11) prepared some transition metal complexes of tetramethylguanidine, and Williams *et al.* (24, 25) titrated several acids in the solvent. Little else has been published.

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The authors report here certain physical properties of tetramethylguanidine and some solubilities and reactions in this solvent medium.

EXPERIMENTAL

Stock 1,1,3,3-tetramethylguanidine (TMG) was obtained from the American Cyanamid Co., Wayne, N. J. It was purified by vacuum distillation from BaO, and the fraction

boiling from 36° to 38° C. at 0.01 mm. was collected. Elemental analysis of the purified TMG gave 52.17% C, 11.24% H, and 36.31% N; theory, 52.14% C, 11.38% H, 36.48% N. To protect the distilled solvent from atmospheric moisture and carbon dioxide, a nitrogen-atmosphere drybox was used for storage and transfers; Drierite- and Ascarite-filled drying tubes protected the solvent during most experimental work.

The density of TMG was measured over about a 20° temperature range with a 50-ml. pycnometer (Sargent S-9285). Refractive index measurements as a function of temperature were made with a Bausch and Lomb Abbé refractometer. The viscosity of TMG was determined using an Ostwald viscometer with liquid samples at 24.8° and 25.2° C., and the two values were averaged.

The specific conductance of the solvent was measured at 24.8° and 25.2° C.; the results were averaged. A Serfass Model RC M15 bridge was used with two conductance cells, one with bright platinum electrodes 10 × 13.5 by 2 mm. apart ($\kappa = 0.1168 \text{ cm.}^{-1}$) and the other with bright platinum electrodes 15 × 20 mm. and separated 3.5 mm. ($\kappa = 0.05143 \text{ cm.}^{-1}$).

The dielectric constant of TMG was measured in a resonant circuit apparatus similar to the Boonton Radio Corp. Q Meter and consisting of a condenser and coil with auxiliary source and detector (20). A number of solvents of known dielectric constants (12) were measured to give a standard curve of frequency *vs.* dielectric constant from which the dielectric constant of TMG was determined.

Infrared spectra were obtained using a Perkin-Elmer Model 21 infrared spectrometer. Proton magnetic resonance spectra were obtained with a Varian Model A-60 spectrometer.

Potentiometric acid-base titrations in aqueous solutions were done with a Model G Beckman pH meter and a glass-calomel electrode system. Glass-silver, silver chloride electrodes were used in argentometric titrations for halide ion. Tetramethylguanidine was determined by nonaqueous titrations in glacial acetic acid and in acetonitrile using glass-silver, silver chloride electrodes and perchloric acid in acetic acid as the titrant.

Tetramethylguanidinium salts were prepared as precipitates by addition of acid to an excess of TMG, followed by filtration. The precipitate was washed with pure TMG and the excess was removed under vacuum at room temperature. Chloride and bromide salts were prepared in this

manner from anhydrous hydrogen halides or the concentrated aqueous acids, whereas the acetate was obtained by addition of glacial acetic acid to TMG. The bicarbonate was prepared by addition of solid or gaseous carbon dioxide to a 1 to 1 TMG-H₂O mixture. All tetramethylguanidinium salts were stored over anhydrous magnesium perchlorate or phosphorus (V) oxide in a vacuum desiccator.

Alkali metal salts used for solubility measurements were stock reagents purified by standard recrystallization and drying methods. In quantitative measurements, triplicate samples of each salt were used. Equilibration of the salt with excess solvent was done by shaking each sample flask for 72 hours in a constant-temperature (25.04° ± 0.04° C.) water bath. Weighed aliquots of saturated solution were dried under vacuum at room temperature for 3 to 5 days to remove excess solvent, and the residue mass was obtained. Residues also were analyzed for alkali metal, generally by flame photometry (22), and for TMG by titration with standard aqueous acid (to pH 5). Solubilities then were calculated in grams of solute per 100 grams of solvent.

Commercial analyses of TMG and its derivatives were done by Alfred Bernhardt Microanalytical Laboratory, Mulheim (Ruhr), West Germany, and by Spang Microanalytical Laboratory, Ann Arbor, Mich.

Because severe eye damage or blindness can result from brief contact of the eye with TMG, safety glasses with side shields should be worn. More detailed toxicity information is available from published reports of the American Cyanamid Co. (1) and from the results of an independent toxicological investigation of the solvent obtained in this work (2).

RESULTS AND DISCUSSION

Physical Constants. Several physical constants of pure, distilled 1,1,3,3-tetramethylguanidine were determined and are listed in Table I, together with some calculated constants.

The heat of vaporization of TMG was calculated from vapor pressure data published by the American Cyanamid Co. (1). However, to obtain a linear relationship between $\log p$ and $1/T$, the assumption was made that the vapor

Table I. Physical Constants for 1,1,3,3-Tetramethylguanidine

| Measured | |
|------------------------------------|--|
| Freezing point | -78° C., glass |
| Boiling point (745 mm.) | 159.5° C. |
| Density, d^{25} | 0.9136 g. ml. ⁻¹ |
| Dielectric constant, D^{25} | 11.5 |
| Refractive index, n_D^{25} | 1.4659 |
| Specific conductance (25° C.) | $9.9 \times 10^{-7} \text{ ohm}^{-1} \text{ cm.}^{-1}$ |
| Viscosity (25° C.) | 1.40 cp. |
| Infrared absorption | |
| $\nu(\text{N-H})$ | 3311 cm.^{-1} |
| $\nu(\text{C=N})$ | 1594 cm.^{-1} |
| Proton magnetic resonance | |
| CH ₃ | 7.38 τ^a |
| NH | 4.83 τ |
| Calculated | |
| Heat of vaporization, ΔH_v | 11.2 kcal. mole ⁻¹ |
| Trouton constant | 25.9 cal. mole ⁻¹ ° K. ⁻¹ |
| Molar refraction, M_r^D | 34.91 cc. moles ⁻¹ |

^a Tetramethylsilane standard = 10.00 τ .

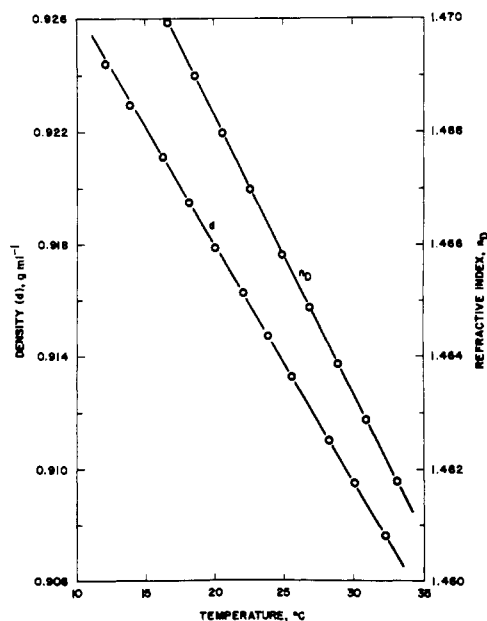


Figure 1. Density and refractive index of 1,1,3,3-tetramethylguanidine as a function of temperature

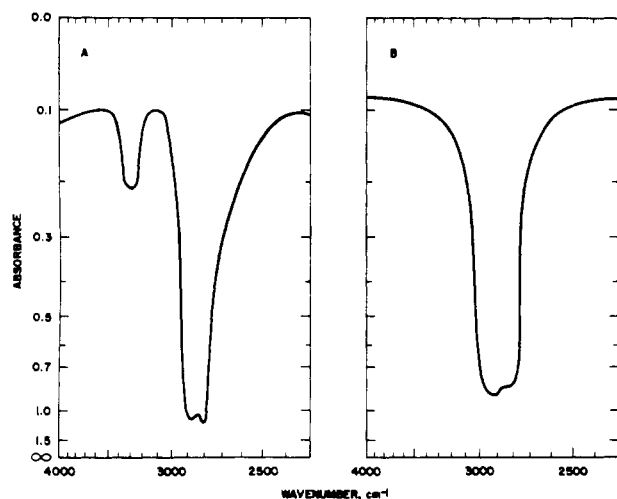


Figure 2. Infrared spectra

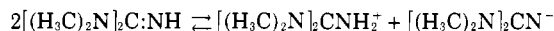
- A. 1,1,3,3-tetramethylguanidine (neat liquid)
 B. 1,1,3,3-tetramethylguanidinium bromide (KBr pellet)

pressure of TMG at 25° is 2.0 mm. rather than 0.2 mm. as reported (typographical error?). This assumption is supported by measurements made in this laboratory. The Trouton constant was determined from the calculated value of ΔH_v and the measured boiling point. The relatively high values for the heat of vaporization and the Trouton constant indicate considerable association in the liquid state. The fact that TMG does not freeze but forms a glass when cooled is further evidence for intermolecular forces in the liquid that are too strong to permit rearrangement into the ordered crystalline state.

The molar refraction of TMG was calculated by the Lorenz-Lorentz equation using the measured value of the refractive index. Both the refractive index and density of TMG were linear with temperature over approximately 20 degrees. Data are plotted in Figure 1.

The estimated error in the determination of the dielectric constant of TMG is $\pm 5\%$, giving $D = 11.5 \pm 0.6$ at 25° C. This value is nearly the same as the constant for ethylenediamine (14.2 at 20° C.) or pyridine (12.3 at 25° C.) (17), and ion-pairing is expected in solutions of electrolytes in TMG.

The observed specific conductance for TMG of 9.9×10^{-7} ohm⁻¹ cm.⁻¹, a tentative upper limit, is about an order of magnitude greater than that for ethylenediamine and is larger by 10^9 than the lowest value obtained for pyridine (17). Caruso, Sears, and Popov (26), in reporting later work on TMG from this laboratory, give $D = 11.00 \pm 0.02$ and a specific conductance range of 5 to 10×10^{-8} ohm⁻¹ cm.⁻¹. Further conductance studies of highly purified solvent are therefore needed, as well as a value for the self-ionization constant of the reaction



The measured viscosity of TMG (1.40 cp. at 25° C.) lies between that of pyridine (0.945 cp. at 20° C.) and ethylenediamine (1.725 cp. at 25° C.) (4). As TMG is cooled, it becomes increasingly viscous and is glassy at -78° C. Very likely a network of hydrogen bonds develops in the solvent as the temperature is lowered.

Infrared absorption bands assigned to stretching vibrations of the N—H and C=N bonds in 1,1,3,3-tetramethylguanidine are 3311 and 1594 cm.⁻¹, respectively (Table I). These assignments are based on the spectrum of the neat liquid using a liquid cell path length of 0.015 mm. The C=N stretching vibration lies some 45 cm.⁻¹ below the minimum of the 1690- to 1640-cm.⁻¹ range generally found in guanidines (15) and this shift probably can be

Table II. Solubilities in 1,1,3,3-Tetramethylguanidine (G./100 g. TMG) at 25° C.

| | Na ⁺ | K ⁺ |
|---|-----------------|----------------|
| ClO ₄ ⁻ | 52 | ... |
| NCS ⁻ | 31 | ... |
| I ⁻ | 21 | ... |
| ClO ₃ ⁻ | 4.0 | 0.14 |
| NO ₃ ⁻ | 1.4 | ... |
| BrO ₃ ⁻ | ... | 0.062 |
| Br ⁻ | 0.68 | 0.058 |
| IO ₃ ⁻ | 0.0058 | ... |
| Cl ⁻ | 0.0041 | 0.0035 |
| C ₂ H ₃ O ₂ ⁻ | 0.0031 | ... |
| HSO ₄ ⁻ | 0.0015 | ... |
| SO ₄ ²⁻ | 0.00054 | ... |

attributed to hydrogen bonding (14). Recently a 1609-cm.⁻¹ band was reported (11) for the C=N absorption in a dilute solution of TMG in cyclohexane. The difference between this observation and the value of 1594 cm.⁻¹ from the present work probably is experimental error.

Our infrared spectrum of liquid TMG compares closely with the Sadtler spectrum (18) except in the N—H stretching region. The sharp N—H band at 3311 cm.⁻¹ (Figure 2, A) is masked in the Sadtler spectrum by a large water band at 3450 to 3200 cm.⁻¹ (7). A spectrum nearly identical to that reported by Sadtler was obtained by us from a freshly prepared 1 to 1 solution of water in TMG.

The two chemical shifts or τ values in the proton magnetic resonance spectrum of 1,1,3,3-tetramethylguanidine agree with its structure. Integration gave a relative NH-to-CH₃ proton ratio of 0.95 to 12 compared with the true ratio of 1 to 12.

Solubilities. Measured solubilities of a number of sodium and potassium salts in 1,1,3,3-tetramethylguanidine are listed in Table II. A comparison of solubilities of some common sodium salts in TMG with published (4) values of solubilities in water, ammonia, and ethylenediamine is given in Table III in units of moles of solute per 10 moles of solvent. In general, solubilities in TMG parallel those in liquid ammonia and in ethylenediamine, but TMG is a somewhat poorer solvent. Solvation was not detected for any of these salts, and apparently TMG does not solvate the solute cations or anions as much as does ammonia or ethylenediamine. The entropy of solution in TMG might be large owing to disruption of the hydrogen bonded liquid structure.

Semiquantitative solubilities (Table IV) were obtained generally by residue weight analysis after single equilibrations. Some of these solubilities no doubt are affected by reaction with the solvent. For instance, ammonium salts undergo solvolysis, transition metal salts form complexes, K₂Cr₂O₇ is slowly reduced by TMG, etc. With some exceptions, Tables II and IV indicate the general order of solubilities to be NH₄ ≈ Li > Na > K and NCS > ClO₄,

Table III. Comparison of Solubilities (Moles Solute/10 Moles Solvent) in Various Solvents at 25° C.

| | H ₂ O | NH ₃ | H ₂ NC ₂ H ₄ NH ₂ | TMG |
|--------------------|------------------|-----------------|---|-----------|
| NaNCS | 3.168 | 4.316 | 6.931 | 4.403 |
| NaClO ₄ | 3.084 | ... | 1.477 | 4.892 |
| NaI | 2.208 | 1.839 | 1.387 | 1.617 |
| NaNO ₃ | 1.939 | 1.955 | 2.368 | 0.1897 |
| NaCl | 1.109 | 0.08802 | 0.03393 | 0.0008079 |

Table IV. Semiquantitative Solubilities in 1,1,3,3-Tetramethylguanidine at Room Temperature

Very Soluble ($\sim > 10$ g./100 g. TMG)
 NH_4NCS , NH_4ClO_4 , NH_4NO_3 , NH_4I , LiNCS , LiNO_3 , LiClO_4 , LiI , LiBr , LiCl , KNCS , $\text{Mg}(\text{ClO}_4)_2$, $\text{Ca}(\text{NO}_3)_2$, $\text{Pb}(\text{NO}_3)_2$, $\text{Co}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4\text{H}_2\text{O}$, $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{H}_2\text{O}$, $\text{Cr}(\text{C}_2\text{H}_3\text{O}_2)_3 \cdot \text{H}_2\text{O}$

Moderately Soluble ($\sim 1 - 10$ g./100 g. TMG)
 $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$, NaHSO_3 , KI , $\text{K}_2\text{Cr}_2\text{O}_7$, $\text{Sr}(\text{NO}_3)_2$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, CoCl_2 , Cu_2Cl_2 , CuNCS , $\text{Ni}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4\text{H}_2\text{O}$, $\text{TMG} \cdot \text{HBr}$, $p\text{-CH}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3\text{H}$

Slightly Soluble ($\sim 0.1 - 1$ g./100 g. TMG)
 NH_4Br , Na_2S , NaNO_2 , KClO_4 , KNCO , H_3BO_3 , $\text{Ba}(\text{NO}_3)_2$, NaOCH_3 , NaOC_2H_5 , $(\text{C}_6\text{H}_5)_4\text{AsCl}$, $(\text{C}_6\text{H}_5)_4\text{AsClO}_4$, $\text{TMG} \cdot \text{HCl}$, $(\text{CH}_3)_3\text{NOH}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, $\text{Cu}(\text{NCS})_2$, citric acid monohydrate

Relatively Insoluble ($\sim > 0.1$ g./100 g. TMG)
 $(\text{NH}_4)_2\text{S}_2\text{O}_8$, NH_4Cl , NH_4HSO_4 , $(\text{NH}_4)_2\text{SO}_4$, $(\text{NH}_4)_2\text{CO}_3$, NH_4F , $\text{LiC}_2\text{H}_3\text{O}_2$, Li_2SO_4 , LiF , LiOH , Li_2CO_3 , $\text{Li}_2\text{C}_2\text{O}_4$, NaOH , NaHCO_3 , KNO_3 , $\text{KC}_2\text{H}_3\text{O}_2$, K_2SO_4 , $\text{Ca}(\text{OH})_2$, $\text{Ba}(\text{OH})_2$, BaCO_3 , BaO , maleic acid

$> \text{NO}_3 > \text{I} > \text{Br} > \text{C}_2\text{H}_3\text{O}_2 > \text{Cl} > \text{SO}_4$. For alkaline earth metal cations, the order is $\text{Ca} > \text{Sr} > \text{Ba}$, although only the nitrates were measured. Of the hydrated transition metal salts, the acetates are the most soluble, followed by the chlorides. Since ammonium and lithium ion compounds are the most soluble, their salts listed in the relatively insoluble group of Table IV give a good indication of the inorganic anions which confer low solubility.

Generally, TMG is a better solvent for organic compounds than for inorganic salts. Table V indicates that TMG is completely miscible with many organic solvents. Perhaps the sheath of methyl groups around the guanidine moiety in TMG contributes to the solubility of organic compounds. The exothermic reactions of Table V are probably acid-base neutralizations.

Reactions. The end product of the hydrolysis of 1,1,3,3-tetramethylguanidine is 1,1-dimethylurea which slowly precipitates from a TMG-water solution at ordinary tem-

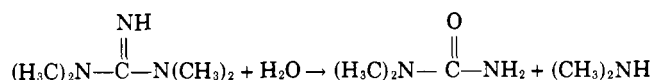
Table V. Miscibility of 1,1,3,3-Tetramethylguanidine with Organic Liquids

| Liquid | Miscibility | Visible Reaction |
|-----------------------|-------------|---------------------|
| Acetic anhydride | Complete | Exothermic |
| Acetone | Complete | None |
| Acetonitrile | Complete | None |
| Benzene | Complete | None |
| n-Butyl ether | Partial | None |
| Carbon tetrachloride | Complete | Slow |
| Cyclohexane | Complete | None |
| Cyclohexanol | Complete | Slightly exothermic |
| Dichloromethane | Complete | Slow |
| N,N-Dimethylformamide | Complete | None |
| p-Dioxane | Complete | None |
| 2-Ethoxyethanol | Complete | Slightly exothermic |
| Ethyl acetate | Complete | None |
| Ethylenediamine | Complete | None |
| Ethyl ether | Complete | None |
| Methanol | Complete | Slightly exothermic |
| Nitrobenzene | Complete | None |
| n-Pentane | Partial | None |
| Petroleum ether | Complete | None |
| Pyridine | Complete | None |
| Tetrahydrofuran | Complete | None |
| Tetramethylurea | Complete | None |

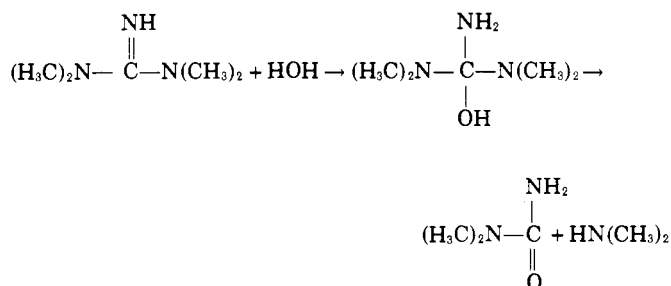
Table VI. Melting Points of Salts of 1,1,3,3-Tetramethylguanidine

| TMGH ⁺ Salt | Melting Point, °C. |
|------------------------------------|--------------------|
| Cl^- | 211-212 |
| Br^- | 184-185 |
| HCO_3^- | 110-113 |
| $\text{C}_2\text{H}_3\text{O}_2^-$ | 90-93 |

peratures but which forms rapidly as an insoluble residue on evaporation of a similar solution. 1,1-Dimethylurea was identified by elemental analysis, melting point, mixed melting point, and infrared spectrum. The over-all hydrolysis reaction probably can be expressed as



A possible mechanism of hydrolysis may involve addition of water to the C=N group, followed by rearrangement to 1,1-dimethylurea and dimethylamine.



Other possible hydrolysis mechanisms may involve such intermediates as tetramethylguanidinium hydroxide (which has never been isolated) (10), tetramethylurea, or 1,1-dimethylguanidine.

Carbon dioxide reacts with moist TMG to precipitate tetramethylguanidinium bicarbonate.

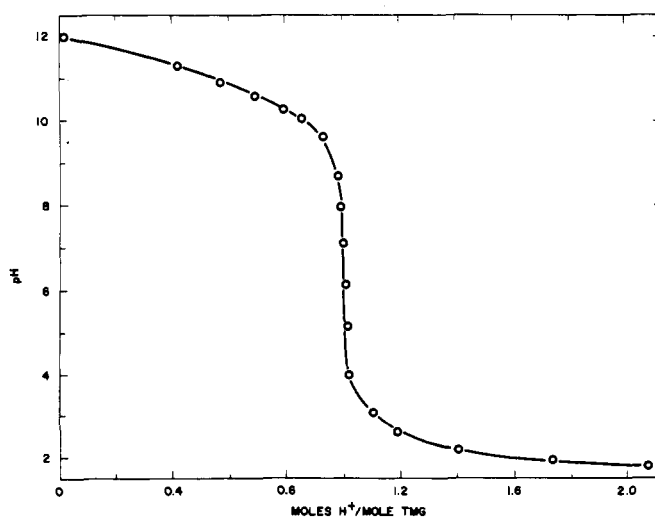


Figure 3. pH-titration of 1,1,3,3-tetramethylguanidine in aqueous media

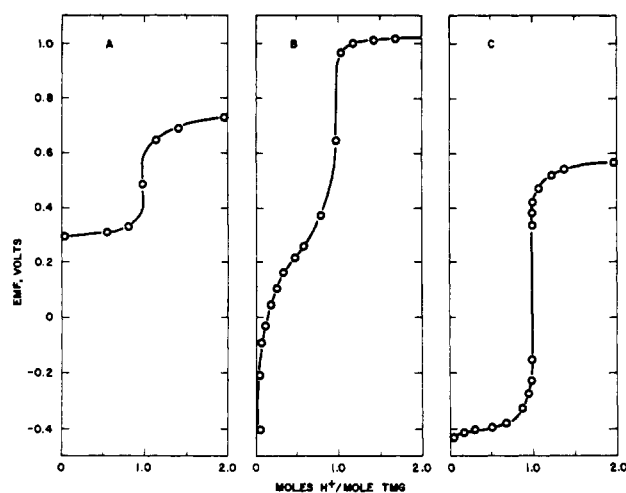
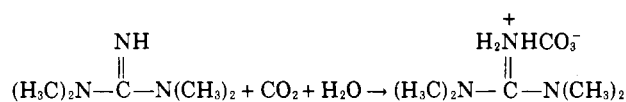


Figure 4. Potentiometric titrations of 1,1,3,3-tetramethylguanidine

- A. in glacial acetic acid
B. in acetonitrile
C. in water (minimal amount)



The necessity for water in the reaction was demonstrated by measurement of the relative weight increase on addition of carbon dioxide to TMG with and without added water. Perhaps because of its hygroscopic nature, elemental analysis of the bicarbonate corresponded to a partial hydrate, $\text{TMGH}^+\text{HCO}_3^- \cdot 0.6 \text{H}_2\text{O}$: Found for $\text{C}_6\text{H}_{15}\text{N}_3\text{O}_3 \cdot 0.6 \text{H}_2\text{O}$: 38.5% C, 8.70% H, 22.2% N; theory 38.3% C, 8.68% H, 22.4% N. Because it is strongly basic [$\text{pK}_a = 13.6$ (3) and 14.06 (13) are reported], TMG reacts vigorously and exothermically with acids to form TMGH^+ salts. No evidence was found in this work for TMGH_2^{2+} salts, in agreement with reported results for other guanidines (3, 23). The chloride, bromide, and acetate salts of TMGH^+ are white, somewhat hygroscopic solids. They were dried by vacuum desiccation over sulfuric acid and their melting points were determined (Table VI). The corresponding iodide salt is reported to melt at 131°C . (3) and to be very hygroscopic. The chloride and bromide were analyzed by aqueous argentometric titration and found to be 1 to 1 TMG-HX salts—viz., 23.13% Cl and 40.40% Br, respectively; theory, 23.37% Cl and 40.75% Br. The acetate salt was not analyzed.

No precipitation occurred when TMG was mixed with 98% sulfuric acid, 72% perchloric acid, or 48% hydrofluoric acid. Concentrated sulfuric acid charred TMG.

Tetramethylguanidine can be titrated potentiometrically with standard acid solutions in either aqueous or nonaqueous media using a glass-calomel electrode system. The typical aqueous titration curve in Figure 3 shows that TMG titrates as a strong monoprotic base. Titrations of TMG in water must be done with a freshly prepared solution to avoid hydrolysis. In fact, if a TMG-water solution stands several hours, a second break in the titration curve occurs at about pH 5 and is probably attributable to dimethylamine.

Other typical potentiometric titration curves of TMG are shown in Figure 4; each indicates only monoprotation. Figure 4, A, represents the titration in glacial acetic acid of TMG with perchloric acid as titrant; Figure 4, B, is similar except that acetonitrile was the solvent. Even stronger protonating conditions are indicated by Figure 4, C, which represents the titration of undiluted TMG with 4.0M HCl. (TMGH^+Cl^- precipitated initially but dissolved on further addition of the aqueous acid.) Addition of excess acid in each of these titrations gave no second inflections in the titration curves.

Since TMG apparently undergoes only monoprotation, as indicated above and by others (3), it is of interest to identify the basic site. Although there is conflicting evidence in the literature whether protonation of ureas and amides occurs on the oxygen or the nitrogen (8, 21), it appears that guanidines protonate predominantly at the imine nitrogen (9), with the resultant positive charge localized on the central carbon atom (6, 16). The latter type of protonation also appears to occur for 1,1,3,3-tetramethylguanidine as shown by comparison of the infrared spectrum of the protonated material with that for the free base. Figure 2, B, shows a portion of the infrared spectrum of 1,1,3,3-tetramethylguanidinium bromide (KBr pellet) where it can be compared directly with the spectrum in Figure 2, A, of liquid TMG. Thus, the N—H stretching vibration at 3311 cm^{-1} in TMG is no longer found in the bromide salt. The explanation may lie, therefore, in protonation of the =NH group to either an $-\text{NH}_2^+$ or a $>\text{C}^+-\text{NH}_2$ group. The $-\text{NH}_2^+$ group absorbs in the "ammonium band" region from 2700 to 2250 cm^{-1} (15), while the triaminocarbonium ion has a broad band at approximately 3300 cm^{-1} , which includes, of course, the $-\text{CH}_3$ stretching absorptions, but no bands in the 2700 to 2250 cm^{-1} region. Thus, the structure of the tetramethylguanidinium ion can perhaps be represented as

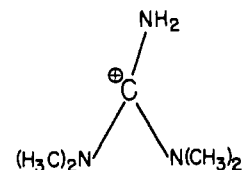


Table VII. Miscellaneous Reactions of 1,1,3,3-Tetramethylguanidine

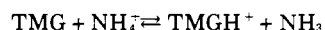
| Reactant | Results, Products |
|---|--|
| Na; K | No reaction (?) |
| Li; LiNH_2 ; NaNH_2 | Decomposition; orange solid |
| LiAlH_4 | Vigorous reaction |
| LiH ; CaH_2 | Slow reaction |
| KMnO_4 | K_2MnO_4 (?) + MnO_2 (vigorous, pyrophoric) |
| $\text{K}_2\text{Cr}_2\text{O}_7$ | Cr^{3+} (slow) |
| NaIO_4 | Yellow solution |
| Ag^+ | Ag |
| Hg_2^{2+} | $\text{Hg} + \text{Hg}^{2+}$ |
| NH_3 | NH_3 |
| CCl_4 ; CHCl_3 ; CH_2Cl_2 | TMGH^+Cl^- |
| CS_2 | Decomposition; orange solid |

A number of other substances reacted with TMG, but in general were studied only on a qualitative or semi-quantitative basis (Table VII). Some gas evolution occurs on addition of metallic sodium or potassium to TMG, but even in the presence of a large excess of solvent, the alkali metal is not consumed. Lithium metal, lithium amide, and sodium amide, on the other hand, decompose the solvent to give unknown red-brown and orange solid products. Treatment of TMG with the hydrides listed in the table gave gas evolution but no products were isolated. Although unsubstituted guanidine is reported (5) to form a monosodium and a disodium compound, the work has never been substantiated. In addition, there is no evidence in the literature for the formation of "guanidides" of any of the alkyl-substituted guanidines.

The reaction of TMG with KMnO_4 is pyrophoric if the permanganate is finely ground. A mixture of green and brown solids is formed which suggests the reduction of MnO_4^- to MnO_4^{2-} and MnO_2 . Potassium dichromate also oxidizes TMG as indicated by the resultant green (Cr^{3+}) solution, but the reaction is slow at room temperature. Sodium periodate apparently oxidizes TMG and may itself be reduced to I_2 as evidenced by the yellow solution which is formed.

Silver(I) salts, if soluble in TMG, are reduced to free silver, especially when heated. The disproportionation of Hg(I) in TMG is similar to that for mercury(I) chloride in ethylenediamine (19).

Ammonium salts on dissolution in TMG invariably evolve ammonia gas; presumably ammonia is the weaker base and ammonium ion acts as an acid in TMG.



Tetramethylguanidine reacts (Table VII) with carbon tetrachloride, chloroform, and dichloromethane analogously to some other basic solvents (4). The decomposition of TMG in carbon disulfide is vigorous and exothermic.

The reactions of TMG listed in Table VII can perhaps be best summarized in terms of some of the problems which they may cause in further study of the solvent. Thus, it was not possible to prepare alkali metal salts of TMG by reaction with the elements, their amides, hydrides, etc. The reactions of TMG with permanganate, dichromate, periodate, and silver(I) indicate that the solvent can be oxidized readily. The reduction of Ag^+ or Hg_2^{2+} to free metal by TMG seems to preclude the use of these salts in titrations, syntheses, or in construction of electrodes. Because of reactions, carbon disulfide or carbon tetrachloride, etc., cannot be conveniently used as spectrophotometric solvents for TMG.

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