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# The Chemistry of TATB and Related Compounds in Sulfuric Acid

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# The Chemistry of TATB and Related Compounds in Sulfuric Acid

Betty W. Harris



## ACRONYMS

| | |
|---|---|
| TATB | 1,3,5-Triamino-2,4,6-trinitrobenzene |
| TADNB | 1,3,5-Triamino-2,4-dinitrobenzene |
| TACDNB | 1,3,5-Triamino-2-chloro-4,5-dinitrobenzene |
| DMSO | N,N-Dimethylsulfoxide |
| HMPA | Hexamethylphosphoric triamide |
| DATNB | 1,3-Diamino-2,4,6-trinitrobenzene |
| TNA | Trinitroaniline |
| TMS | Tetramethylsilane |

# THE CHEMISTRY OF TATB AND RELATED COMPOUNDS IN SULFURIC ACID

by

Betty W. Harris

## ABSTRACT

Information on the chemical properties of 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) in $H_2SO_4$ is presented. The activation energy of the protonation process is 5.92 kcal/mole. The heat of reaction, $\triangle H$, is approximately 0.8 kcal/mole. Cryoscopic and conductance measurements of 1,3,5-triamino-2,4-dinitrobenzene (TADNB), 1,3,5-triamino-2-chloro-4,5-dinitrobenzene (TACDNB), and TATB were compared to measurements of model compounds. The source and number of hydrogen atoms attached to basic groups and to the ring were determined. At a concentration of 0.1 M in $H_2SO_4$, TATB, TADNB, and TACDNB exhibited two basic reacting sites per compound. Reacting sites are concentration dependent and protons are donated from $H_2SO_4$.

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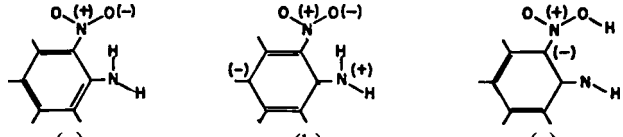
## I. INTRODUCTION

This report is the second part of a preliminary study to evaluate the chemical properties of TATB, its intermediate products, and its impurities in different solvent systems. These data are needed to develop an assay for TATB. Carbon-13 nuclear magnetic resonance ($^{13}C$ NMR) spectroscopy was used in the previous study to determine how protonation and solvation were responsible for the dissolution of TATB in $H_2SO_4$, the most successful solvent.[1] This study uses $^{13}C$ NMR spectroscopy data and cryoscopic and conductance measurements to determine the source and number of additional hydrogen atoms attached to the solute in the TATB/$H_2SO_4$ system.

An analysis of the crystal structure of TATB reveals that many of its unusual properties (for example, a melting point of 450°C and insolubility in most solvents) are caused by a strong matrix of intermolecular hydrogen bonds. Resonance forms such as (b) and (c) below are important, but (a) is not an essential contributor.[2] Methods for the analyses of solid TATB have not been suitable for assaying.

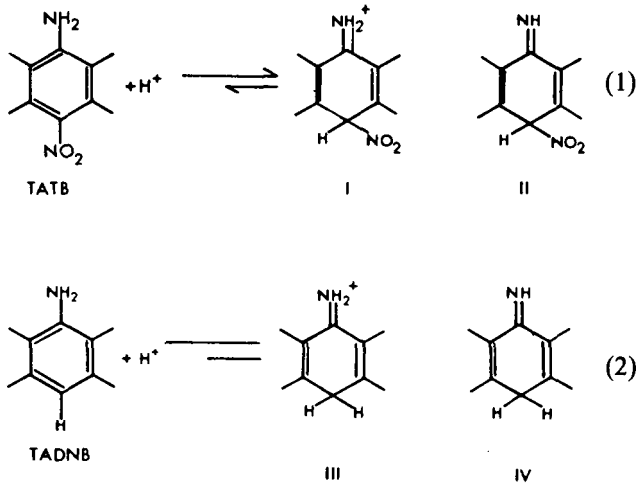


(a) (b) (c)

## II. RESULTS AND DISCUSSION

### A. Carbon-13 NMR Analyses

Carbon-13 NMR analyses of TATB and related compounds have shown that when dissolved in $H_2SO_4$, TATB and TADNB assume a cyclohexadienyl structure with an additional proton at $C_4$ of TATB and $C_6$ of TADNB.[1] Other nitroaniline compounds retain this aromatic structure and become protonated at the amine group, except DATNB, which is unaffected by the solvent. Carbon-13 NMR results for TATB/$H_2SO_4$ and



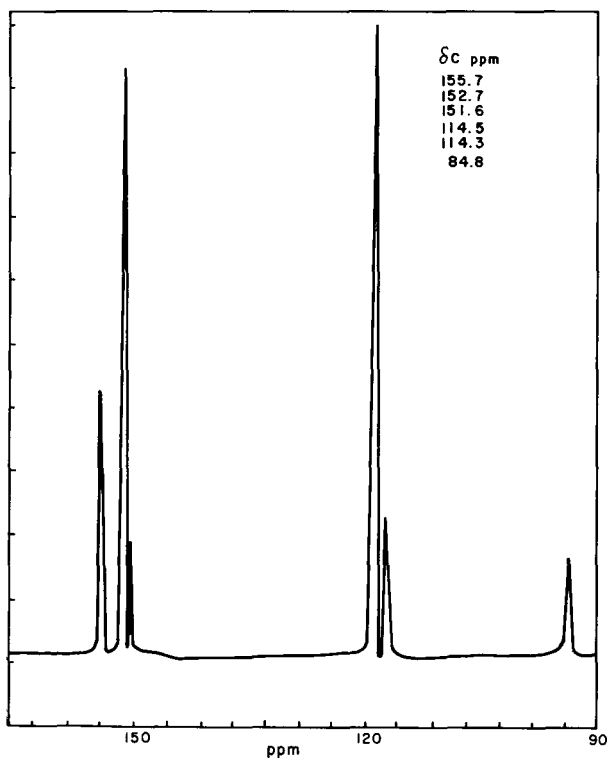




Fig. 1.
Carbon-13 NMR decoupled spectrum of TATB in concentrated $H_2SO_4$.

TADNB/$H_2SO_4$ are shown in Eqs. (1) and (2) and Figs. 1 and 2. The $^{13}C$ NMR splitting patterns of the carbons bearing the hydrogen atoms confirm the presence of the hydrogen atoms (Figs. 3 and 4). What is the origin of the protons? Are they donated from the solvents, forming

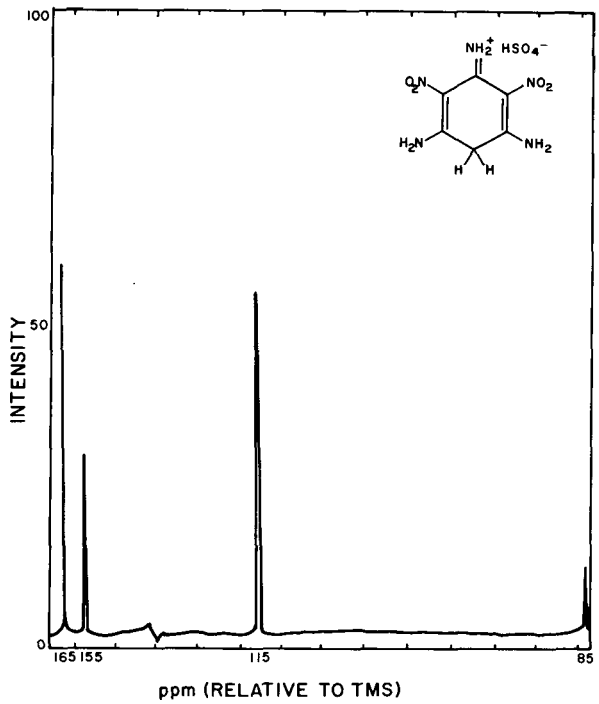



Fig. 2.
Carbon-13 NMR decoupled spectrum of TADNB in concentrated $H_2SO_4$ at 27°C.

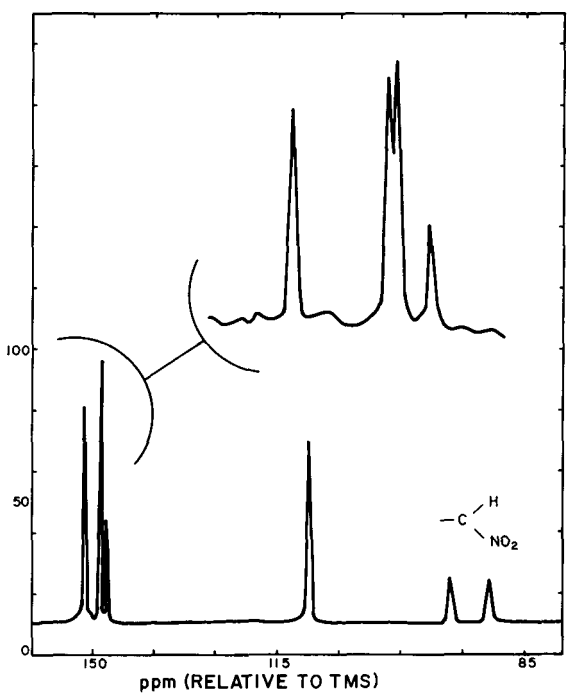



Fig. 3.
Carbon-13 NMR coupled spectrum of TATB in concentrated $H_2SO_4$.

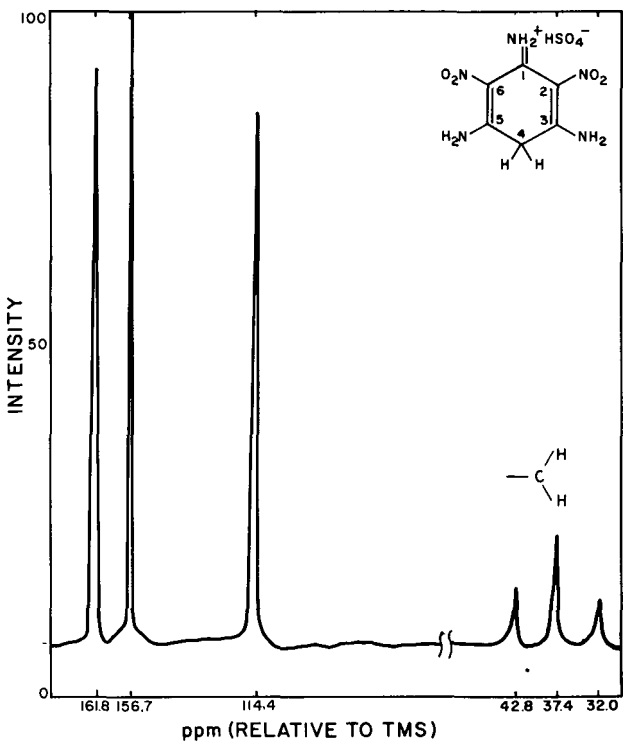



Fig. 4.
Carbon-13 NMR coupled spectrum of TADNB in concentrated $H_2SO_4$ at 25°C.

structures I and III, or do they migrate from the amine group, forming structures II and IV?

Neither $^{13}C$ NMR nor $^{15}N$ NMR spectroscopy completely characterized the C = NH group. However, assignments of 155.7 ppm and 161.8 ppm for the imino carbon in TATB and TADNB, respectively, were in agreement with the assignments of the imino carbons in 1-nitroguanyl-1,3,5-dimethylpyrazole (158.7 ppm) and arginine hydrochloride (157.7 ppm). We assumed that the rapid exchange between the proton of the imino group and those of the solvent caused the imino $^{15}N$ resonance in TATB and TADNB to appear as singlets.

Carbon-13 NMR linewidth data from $C_4$ structure I [Eq. (1)] were used to determine the activation energy of the TATB/$H_2SO_4$ system. If the rate of exchange of the proton at $C_4$ obeys first-order kinetics, an activation energy of 5.92 kcal/mole can be calculated from the slope of the semilogarithmic plot of the rate constants vs the reciprocal of the absolute temperature. Rate constants at various temperatures were calculated from linewidth data using published procedures.[3] The relationship between the change in linewidth (at half height) of the $C_4$ absorption of TATB in $H_2SO_4$ and the rate of exchange (k) of the proton at this position with temperature (T) is shown in Table I. The graph of these data (Fig. 5) is consistent with observations from $^{13}C$ NMR chemical shift data. At approximately 304.15 K, a change in mechanism is evident.

Activation energies of 5-6 kcal/mole imply that the rate-determining step in the reaction shown in Eq. (1) is the diffusion of reactant or product molecules.[4]

Peak ratios from the TATB spectrum were determined from peak height changes with temperature. We calculated an average heat of reaction, $\triangle H$, of 0.8 kcal/mole

TABLE I

LINEWIDTHS[a] AND RATE CONSTANTS AS FUNCTIONS OF TEMPERATURE

| 1000/T ($K^{-1}$) | 1000/$\pi_{1/2}$ (s) | (100)k ($s^{-1}$) | (ln K) |
|---|---|---|---|
| 3.69 | 2.20 | 5.5 | 6.3099 |
| 3.60 | 2.53 | 6.3 | 6.4457 |
| 3.56 | 2.97 | 7.4 | 6.6067 |
| 3.48 | 3.77 | 9.4 | 6.8459 |
| 3.44 | 3.89 | 9.7 | 6.8773 |
| 3.38 | 4.73 | 11.8 | 7.0733 |
| 3.22 | 5.06 | 12.7 | 7.1468 |
| 3.14 | 5.62 | 14.0 | 7.2442 |
| 2.99 | 0.253 | --- | --- |

[a]Linewidth at half height, $\nu_{1/2} = 1/\pi \cdot T_2'$, where $T_2'$ = effective transverse relaxation time.

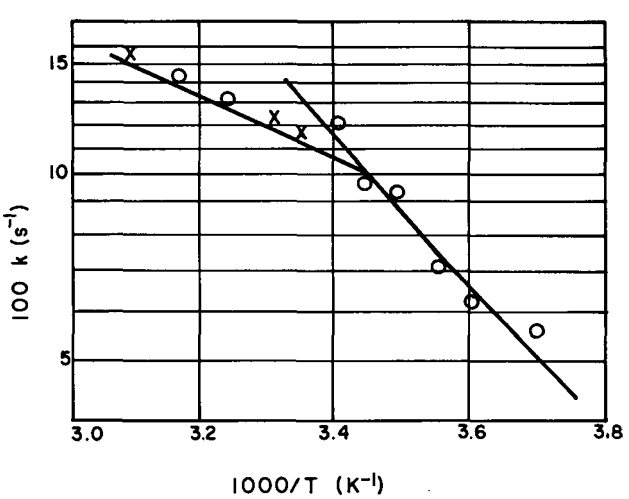



Fig. 5.
Rate constants vs temperature.

(Tables II-IV). These data suggest little difference in the stability of the reactants and products.

### B. Conductance and Cryoscopic Measurements

We attempted to use a simple conductivity experiment to distinguish between structures I and II [Eq. (1)]. A conductivity cell was constructed by R. Rowher, Los Alamos National Laboratory Group WX-2. The cross section of the cell was 1.0 $cm^2$ and its length was 11.5 cm. The cell constant was 12.3 $cm^{-1}$ when measured in 0.01 M KCl and was 2.2 $cm^{-1}$ when measured in concentrated $H_2SO_4$ (96-98%). Several solutions were prepared with varying amounts of TATB dissolved in 25 $cm^3$ of concentrated $H_2SO_4$. The equivalent conductance $\Omega$ was measured using a YSI* Model 31 conductivity bridge. The values obtained immediately after mixing were slightly higher than those obtained after 2 wk (Table V and Fig. 6). The conductance tended to decrease as the concentration increased. Both the formation of aggregates of ions and an increase in viscosity of the solution would cause the mobility of the ions to be reduced and the conductance to be less. Another factor affecting conductance is the increase in hydrogen bonding with concentration, which can reduce the number of molecules of $H_2SO_4$ available to be ionized. The only significant ionization of the solvent is shown in Eq. (5). It

*Yellow Springs Instrument Co., Yellow Springs, Ohio.

TABLE II

CHANGE IN RATIO OF UNPROTONATED TO PROTONATED FORMS OF TATB[a] AT VARYING TEMPERATURES[b]

| 1000/T ($K^{-1}$) | Unprotonated TATB / Protonated TATB |
|---|---|
| 3.55 | 0.1972 |
| 3.50 | 0.2480 |
| 3.42 | 0.2854 |
| 3.35 | 0.2230 |
| 3.32 | 0.2520 |
| 3.22 | 0.1312 |
| 3.19 | 0.2307 |
| 3.10 | 0.2824 |

[a]Los Alamos Group WX-3 Cordova Blend No. 7712.
[b]$\Delta H = -0.773$ kcal/mole.

TABLE III

CHANGE IN RATIO OF UNPROTONATED TO PROTONATED FORMS OF TATB[a] AT VARYING TEMPERATURES[b]

| 1000/T ($K^{-1}$) | Unprotonated TATB / Protonated TATB |
|---|---|
| 3.61 | 0.2558 |
| 3.46 | 0.2883 |
| 3.88 | 0.3197 |
| 3.26 | 0.2133 |
| 3.13 | 0.2700 |
| 3.14 | 0.3233 |
| 3.04 | 0.3068 |

[a]Los Alamos Group WX-3 Cordova Blend No. 7705.
[b]$\Delta H = -0.758$ kcal/mole.

TABLE IV

CHANGE IN RATIO OF UNPROTONATED TO PROTONATED FORMS OF TATB[a] AT VARYING TEMPERATURES[b]

| 1000/T ($K^{-1}$) | Unprotonated TATB / Protonated TATB |
|---|---|
| 3.59 | 0.2581 |
| 3.52 | 0.2521 |
| 3.47 | 0.2269 |
| 3.34 | 0.3230 |
| 3.27 | 0.3045 |
| 3.12 | 0.2626 |
| 3.04 | 0.2857 |

[a]This is a laboratory sample prepared by Donald Ott of Los Alamos Group WX-2.
[b]$\Delta H = -0.773$ kcal/mole.

TABLE V

THE EFFECT OF CONCENTRATION ON THE EQUIVALENT CONDUCTANCE OF TATB IN CONCENTRATED $H_2SO_4$ AT 25°C

| TATB/25 cm³ $H_2SO_4$ | Conductance[a] ($\Omega^{-1}cm^{-1}$) | Conductance After 2 wk[a] ($\Omega^{-1}cm^{-1}$) |
|---|---|---|
| 0.0 | 1.98 | 1.82 |
| 0.5 | 1.94 | 1.80 |
| 1.0 | 1.71 | 1.78 |
| 1.5 | 1.86 | 1.74 |
| 2.0 | 1.85 | 1.72 |
| 2.5 | 1.71 | 1.68 |
| 3.0 | 1.68 | 1.73 |
| 4.0 | 1.52 | 1.54 |
| 5.0 | 1.50 | 1.47 |
| 5.3 | 1.51 | 1.48 |

[a]Numbers to be multiplied by $10^{-2}$; $\Omega$ = ohms$^{-1}$.

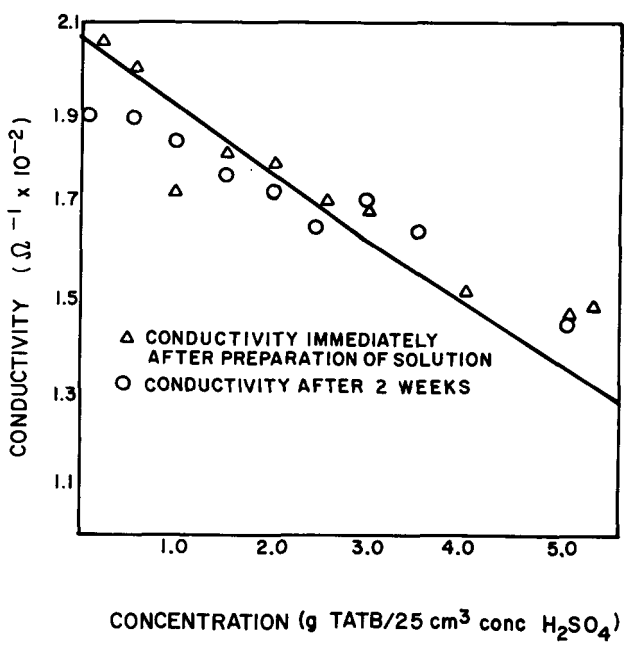



Fig. 6.
Conductivity of TATB in $H_2SO_4$.

was not necessary to make corrections for self-ionization by self-dehydration and autoprotolysis [Eqs. (3) and (5)].

$$2H_2SO_4 \rightleftharpoons H_3SO_4^+ + HSO_4^-;$$

$$K_b = \frac{1 \text{ mole}}{\text{kg}} . \qquad (3)$$

$$2H_2SO_4 \rightleftharpoons H_3O^+ + HS_2O_7^-;$$

$$K_a = 1.4 \times 10^{-2} \frac{\text{mole}}{\text{kg}} . \qquad (4)$$

$$H_3SO_4^+ + HS_2O_7^- \rightleftharpoons H_2SO_4 + H_2S_2O_7;$$

$$K_{ap} = 1.7 \times 10^{-4} \frac{\text{mole}^2}{\text{kg}^2} . \qquad (5)$$

$$H_2O + H_2SO_4 \rightleftharpoons H_3O + HSO_4^-;$$

$$K_{id} = 3.5 \times 10^{-5} \frac{\text{mole}^2}{\text{kg}^2} . \qquad (6)$$

In a more detailed cryoscopic and conductance study, TATB, TACDNB, and TADNB were compared to model compounds, and the extent of protonation as a function of concentration was determined.[5]

The dissociation products from the reactions illustrated in Eqs. (3)-(6) lower the freezing point of 100% $H_2SO_4$ from 10.625°C to 10.365°C.[6] The self-dissociation products and the effect of the dissolved solute on the equilibria expressed in Eqs. (3)-(6) were taken into consideration in determining $V$, the number of moles of particles (molecules or ions) produced in solution by 1 mole of solute. This relationship is expressed as

$$V = \frac{\theta}{\text{km}} , \qquad (7)$$

where k is the molal freezing point depression constant, m is the molality of the solution, and θ is the freezing point depression.

A more accurate expression of $V$ is

$$V = \frac{\theta(1 + 0.002\theta)}{6.12\ [m\text{-}(m/m_d)]}\ , \qquad (8)$$

where $m_d$ is the total molality of solution containing dissociation products, $m/m_d$ is a correction factor for the dissociation products, and θ is the actual freezing point depression calculated from $T_o$ (10.625°C) and the corrected freezing point of the solution, T. The corrected freezing points of solvents and solutions are obtained by adding ΔT to the observed freezing points.

The experimentally determined freezing point, $T_e$; the corresponding freezing point depression, $\theta_e$; and the amount of supercooling, S, were used to calculate T.

$$\Delta T = 0.03S\theta_e. \qquad (9)$$

The stoichiometric concentration of $HSO_4^-$ obtained from conductance measurements was plotted vs the concentration of each self-dissociation product. Values for $m_d$ were obtained from these plots (Table VI).[6] Approximate $V$ values for TATB, TACDNB, and TADNB, for concentrations of approximately 0.1 M, are 4, 5, and 4, respectively. As the concentration decreases, the $V$ values increase.

As shown in Eq. (3), the bisulfate ion is produced from the self-dissociation of $H_2SO_4$. In solutions of any base, the contribution to the conductivity of all other ions, compared to $HSO_4^-$, is negligibly small, affording a means of determining the number γ of $HSO_4^-$ ions produced per molecule of solute. At low concentrations, the reaction illustrated by Eq. (3) is not suppressed, and solutions of equal concentration will have equal conductance. Binary electrolytes such as $KHSO_4$ were used as standards. The quantity γ will be the ratio $[HSO_4^-]/m_s$, where $m_s$ is the stoichiometric molality of the solute in a solution whose conductance corresponds to a known stoichiometric molality of the hydrogen sulfate ion, $HSO_4^-$. Using data from Table VI, we plotted $[HSO_4^-]_s$ vs the specific conductance of standard $KHSO_4$ solutions.[7] Then we plotted the specific conductance of solutions of TNA, TATB, TADNB, and TACDNB and obtained the corresponding $[HSO_4^-]_s$ values. Table VII gives the solute; the molality of the solution, $m_s$; the specific conductance of the solution, L; the corresponding molality of the $HSO_4^-$; and γ.

In addition to finding the γ values for solutions of TNA, TATB, TADNB, and TACDNB, we obtained molar conductances μ at 25°C for each solute for comparison with molar conductances of dibasic, tribasic, and tetrabasic solutes, 1,2-benzenediamine, $N_2O_4$, and hexamethylenetetramine, respectively.[8] The molar conductance is calculated using the relationship,

TABLE VI

$V$ VALUES FOR TNA, TATB, TADNB, AND TACDNB SOLUTIONS

| Solute | m | $(HSO_4^-)_s$ | $m_d$ | θ | $V$ |
|---|---|---|---|---|---|
| TNA | 0.2096 | 0.2325 | 0.01440 | 3.137 | 2.38 |
| TNA | 0.1023 | 0.151 | 0.01559 | 2.093 | 3.20 |
| TATB[a] | 0.1026 | 0.171 | 0.01513 | 2.375 | 3.65 |
| TATB[a] | 0.0506 | 0.128 | 0.01607 | 1.765 | 5.40 |
| TATB[b] | 0.0126 | 0.170 | 0.01518 | 2.159 | 3.31 |
| TATB[b] | 0.0506 | 0.104 | 0.01696 | 1.338 | 4.00 |
| TATB[b] | 0.0252 | 0.061 | 0.01992 | 0.842 | 4.68 |
| TADNB | 0.1018 | 0.223 | 0.01446 | 2.651 | 4.14 |
| TADNB | 0.0505 | 0.154 | 0.01555 | 1.586 | 4.84 |
| TADNB | 0.0251 | 0.096 | 0.01733 | 1.052 | 6.15 |
| TACDNB | 0.1025 | 0.258 | 0.01422 | 3.197 | 4.99 |
| TACDNB | 0.0506 | 1.151 | 0.01559 | 1.638 | 4.99 |
| TACDNB | 0.0262 | 0.100 | 0.01718 | 0.974 | 5.43 |

[a]Solvent fp of 10.288°C and L of 0.01015 $\Omega^{-1}cm^{-1}$.
[b]Solvent fp of 10.342°C and L of 0.01030 $\Omega^{-1}cm^{-1}$.

TABLE VII

GAMMA VALUES FOR TNA, TATB, TADNB, AND TACDNB SOLUTIONS

| Solute | $m_s$ | L | $[HSO_4^-]s$ | γ |
|---|---|---|---|---|
| TNA | 0.2096 | 0.03761 | 0.2325 | 1.11 |
| TNA | 0.1023 | 0.02754 | 0.151 | 1.48 |
| TATB[a] | 0.1026 | 0.03080 | 0.171 | 1.67 |
| TATB[a] | 0.0506 | 0.02555 | 0.128 | 2.53 |
| TATB[b] | 0.1026 | 0.03068 | 0.170 | 1.66 |
| TATB[b] | 0.0506 | 0.02225 | 0.104 | 2.05 |
| TATB[b] | 0.0252 | 0.01636 | 0.061 | 2.42 |
| TADNB | 0.1018 | 0.03665 | 0.223 | 2.19 |
| TADNB | 0.0505 | 0.02774 | 0.154 | 3.05 |
| TADNB | 0.0251 | 0.02115 | 0.096 | 3.82 |
| TACDNB | 0.1025 | 0.04050 | 0.258 | 2.52 |
| TACDNB | 0.0506 | 0.02746 | 0.151 | 2.98 |
| TACDNB | 0.0262 | 0.02177 | 0.100 | 3.82 |

[a]Solvent fp of 10.288°C and L of 0.01015 $\Omega^{-1}$ $cm^{-1}$.
[b]Solvent fp of 10.342°C and L of 0.01030 $\Omega^{-1}$ $cm^{-1}$.

$$\mu = \frac{1000L}{w\rho} , \qquad (10)$$

where L is the specific conductance, w is moles of solute per kilogram of solution, and ρ is the density of the solution. The product, wρ, is equal to the concentration of the solute expressed in molarity. Where density measurements were not made, we assumed the densities of the solutions were the same as the density of pure $H_2SO_4$ (1.8271 g/$cm^3$). Values of molar conductances for solutions of bases with a $HSO_4^-$ ion concentration less than 0.1 M are unreliable unless a correction is made for the incomplete repression of the self-dissociation of the solvent. However, in this instance, all solutions had a $HSO_4^-$ molarity greater than or equal to 0.1 M. Table VIII gives the solute and w, ρ, M, and μ values. The molar conductance decreases rapidly as concentration increases. Table IX lists the molalities and corresponding molar conductances for solutions of aniline, 1,2-benezenediamine, $N_2O_4$, and hexamethylenetetramine.[8]

We performed a careful study of the freezing point and specific conductance of $H_2SO_4$ to determine its purity. Table X gives the freezing points, and Table XI (data taken from Ref. 7) gives the specific conductances of solutions of $H_3O^+HSO_4^-$ and $H_2S_2O_7$ in 100% $H_2SO_4$ over the concentration ranges pertinent to our study. From these data, we can estimate that the molality of the solvents used in our studies ranged from less than 0.01 molal concentrations of either $H_2O$ or $SO_3$ to 0.040 molal concentration of $H_2O$ or 0.050 molal concentration of $SO_3$. In three instances our specific conductances are 1-2% lower than the minimum value for 100% $H_2SO_4$, which suggests that 1-2% is a more realistic precision range for our conductance measurements than the relative precision range of 0.1-0.5% given in Sec. IV.

Table XII gives $V$ values and γ values for the solutions and upper limit estimates on the molality of impurities. We assumed the main impurity was $H_2O$, the most likely candidate.

## III. CONCLUSIONS

Tables XIII and XIV summarize the cryoscopic and conductance experimental results. Table XIV has been corrected for $H_2O$ impurity. Even though very dilute solutions seem to give the best results, these cannot be compared with the $^{13}C$ NMR data obtained from the Varian CFT-20 NMR spectrometer for assay purposes because of concentration constraints. We chose to

TABLE VIII

MOLAR CONDUCTANCES OF TNA, TATB, TADNB, AND TACDNB AT 25°C

| Solute | w | ρ | M | μ |
|---|---|---|---|---|
| TNA | 0.2000 | 1.8311 | 0.3662 | 102.7 |
| TNA | 0.1000 | 1.8297 | 0.1830 | 150.5 |
| TATB | 0.1000 | 1.8361 | 0.1836 | 167.7 |
| TATB | 0.1000 | 1.8361 | 0.1836 | 167.1 |
| TATB | 0.0500 | 1.8302 | 0.0915 | 279.2 |
| TATB | 0.0500 | 1.8302 | 0.0915 | 243.2 |
| TATB | 0.0250 | 1.8271 | 0.457 | 358.0 |
| TADNB | 0.0996 | 1.8271 | 0.1820 | 201.3 |
| TADNB | 0.0500 | 1.8271 | 0.0914 | 303.5 |
| TADNB | 0.0250 | 1.8271 | 0.0457 | 462.8 |
| TACDNB | 0.1000 | 1.8271 | 0.1827 | 221.7 |
| TACDNB | 0.0500 | 1.8271 | 0.0914 | 300.4 |
| TACDNB | 0.0260 | 1.8271 | 0.0475 | 458.2 |

TABLE IX

MOLAR CONDUCTANCE OF ANILINE, 1,2-BENZENEDIAMINE, $N_2O_4$, AND HEXAMETHYLENETETRAMINE AT 25°C

| Solute | M | μ |
|---|---|---|
| Aniline | 0.1 | 155 |
| Aniline | 0.2 | 120 |
| Aniline | 0.3 | 102 |
| Aniline | 0.4 | 91.5 |
| 1,2-Benzenediamine | 0.05 | 306 |
| 1,2-Benzenediamine | 0.10 | 236 |
| 1,2-Benzenediamine | 0.15 | 201 |
| 1,2-Benzenediamine | 0.20 | 187 |
| 1,2-Benzenediamine | 0.30 | 153 |
| 1,2-Benzenediamine | 0.40 | 130 |
| $N_2O_4$ | 0.033 | 453 |
| $N_2O_4$ | 0.066 | 336 |
| $N_2O_4$ | 0.100 | 296 |
| $N_2O_4$ | 0.133 | 268 |
| Hexamethylenetetramine | 0.025 | 616 |
| Hexamethylenetetramine | 0.050 | 454 |
| Hexamethylenetetramine | 0.075 | 388 |
| Hexamethylenetetramine | 0.100 | 349 |

TABLE X

FREEZING POINTS OF $H_2SO_4$ SOLUTIONS OF $H_3O^+HSO_4^-$ AND $H_2S_2O_7$

| Molality | fp, $H_3O^+HSO_4^-$ | fp, $H_2S_2O_7$ |
|---|---|---|
| 0.000 | 10.371 | 10.371 |
| 0.005 | 10.364 | 10.366 |
| 0.010 | 10.346 | 10.351 |
| 0.015 | 10.316 | 10.329 |
| 0.020 | 10.280 | 10.305 |
| 0.025 | 10.237 | 10.276 |
| 0.030 | 10.194 | 10.248 |
| 0.035 | 10.146 | 10.214 |
| 0.040 | 10.094 | 10.182 |
| 0.050 | 9.993 | 10.118 |

TABLE XI

SPECIFIC CONDUCTANCES AT 25°C OF $H_2SO_4$ SOLUTIONS OF $H_3O^+HSO_4^-$ AND $H_2S_2O_7$

| Molality | L, $H_3O^+HSO_4^-$ | L, $H_2S_2O_7$ |
|---|---|---|
| 0.000 | 0.01044 | 0.01044 |
| 0.01 | 0.01058 | 0.01064 |
| 0.02 | 0.01117 | 0.01105 |
| 0.03 | 0.01209 | 0.01154 |

TABLE XII

RESULTS OF CRYOSCOPIC AND CONDUCTANCE EXPERIMENTS

| Molality of Solute | Upper Limit of Molality of $H_2O$ Impurity | $V$ | $\gamma$ |
|---|---|---|---|
| 0.2096 m TNA | 0.02 m | 2.38 | 1.11 |
| 0.1023 m TNA | 0.02 m | 3.20 | 1.48 |
| 0.1026 m TATB[a] | 0.02 m | 3.65 | 1.67 |
| 0.0506 m TATB[a] | 0.02 m | 5.40 | 2.53 |
| 0.1026 m TATB[b] | 0.01 m | 3.31 | 1.66 |
| 0.0506 m TATB[b] | 0.01 m | 4.00 | 2.05 |
| 0.0252 m TATB[b] | 0.01 m | 4.68 | 2.42 |
| 0.1018 m TADNB | 0.04 m | 4.14 | 2.19 |
| 0.0505 m TADNB | 0.04 m | 4.84 | 3.05 |
| 0.0251 m TADNB | 0.04 m | 6.16 | 3.82 |
| 0.1025 m $T_4A$ | 0.01 m | 4.99 | 252 |
| 0.0506 m $T_4A$ | 0.01 m | 4.99 | 2.98 |
| 0.0262 m $T_4A$ | 0.01 m | 5.43 | 3.82 |

[a]Solvent fp of 10.288°C and L of 0.01015 $\Omega^{-1}$ $cm^{-1}$.
[b]Solvent fp of 10.342°C and L of 0.01030 $\Omega^{-1}$ $cm^{-1}$.

TABLE XIII

MOLAR CONDUCTANCE OF TATB, TADNB, AND TACDNB IN $H_2SO_4$ AT 25°C

| Solute | Molarity | Conductance |
|---|---|---|
| TACDNB | 0.0914 | 300.4 |
| | 0.1827 | 221.7 |
| TADNB | 0.0914 | 303.5 |
| | 0.1820 | 201.3 |
| TATB | 0.0915 | 279.2 |
| | 0.1836 | 167.1 |

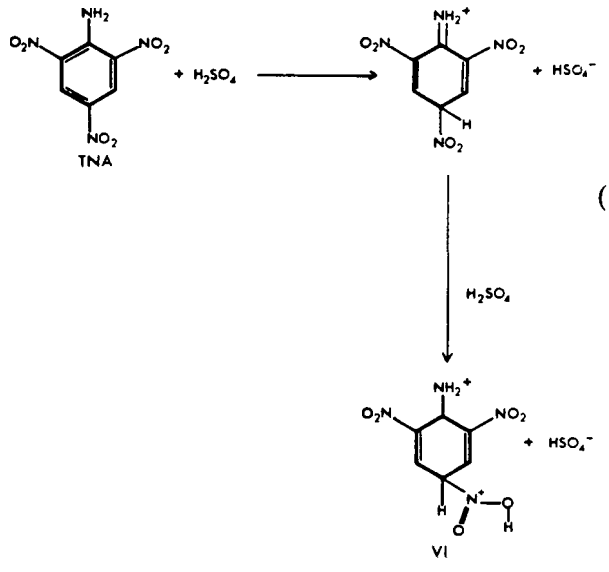
TABLE XIV

CRYOSCOPIC AND CONDUCTANCE EXPERIMENTS CORRECTED FOR THE IMPURITY $H_2O$[a]

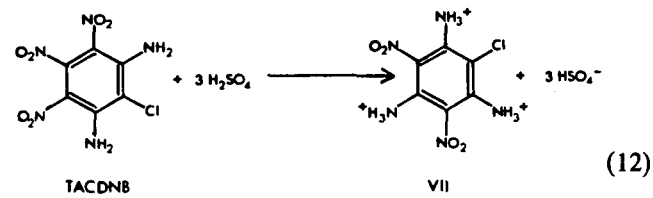
| Compound | $m_s$ | $m_{H_2O}$ | $V$ | $\gamma$ |
|---|---|---|---|---|
| TNA | 0.1023 | 0.02 | 2.8 | 1.0 |
| TACDNB | 0.1025 | 0.01 | 5.0 | 2.4 |
| TADNB | 0.1018 | 0.02/0.04 | 4.1 | 1.9 |
| TATB | 0.01026 | 0.02 | 3.3 | 1.5 |

[a]Concentrations approximately 0.1 M and temperature 25°C.

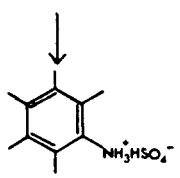
compare the 0.1 molal solutions of the model compounds with the aminonitrobenzene derivatives of interest. With the exception of the model compound TNA, other compounds seem to generate at least two $HSO_4^-$ ions per mole of solute. The strong evidence that TACDNB generates three bisulfate ions per mole of solute also corroborates the $^{13}C$ NMR data. The numbers of moles of particles in solution (molecules and/or ions) for TNA, TACDNB, TADNB, and TATB are 3, 5, 4, and 3, respectively. The following equations illustrate these results.

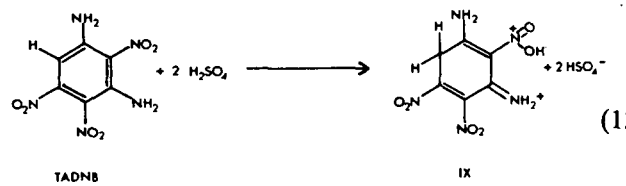



(11)

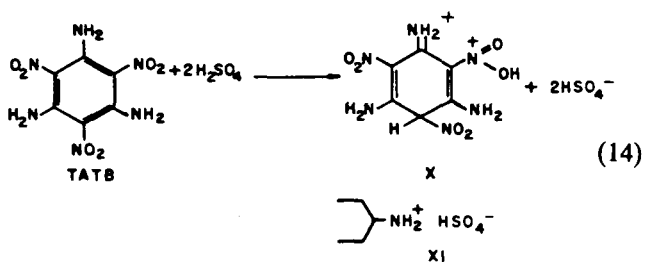



(12)




(13)




(14)

We concluded that $H_2SO_4$ provides the protons attached at the amino and nitro groups and also at the ring in Eqs. (11)-(14). The extent of protonation depends upon the concentration of the solvent. Acid solutions with $H_2SO_4$ concentrations of 96-98% are better proton donors than 100% $H_2SO_4$, and structures VIII and XI are not strong contributors. Therefore, in $H_2SO_4$, TATB and TADNB exist as structures I and III, respectively.

## IV. CONDUCTANCE MEASUREMENTS

### A. Reagents

Sulfuric Acid: VWR reagent grade, A.C.S., 96-98% $H_2SO_4$

Sulfur Trioxide: Sargent-Welch ampules (Cat. No. SC15137-00/2LB)

Potassium Chloride: Mallinckrodt, U.S.P.

White mineral oil for constant temperature bath for conductivity studies: Sargent-Welch mineral oil (inhibited), Cat. No. SC13639

TNA, TATB, TADNB, and TACDNB

### B. Procedures

Figures 7 and 8 show views of the conductivity cell. When the cell within the air jacket is filled to 6 cm, the volume of the solution equals approximately 50 ml. Two pairs of platinum electrodes are incorporated into the cell. The upper pair (No. 1) and the lower pair (No. 2) are each 2.5 cm apart. Each No. 1 electrode has a radius of about 0.28 cm; each No. 2 electrode has a radius of about 0.16 cm. Platinum wire leads (insulated with glass inside the cell) extend from the electrodes to the glass tubes along the outside of the air jacket, where contact to external leads is made with mercury. By setting the cell on either an electric-powered or water-powered magnetic stirrer, we can stir the solution with a Teflon-coated magnetic-stir bar.

The cell constant for both pairs of electrodes was determined using standard KCl solutions (7.4194 g KCl/kg of solution with L = 0.012856 $\Omega^{-1}$ $cm^{-1}$ at

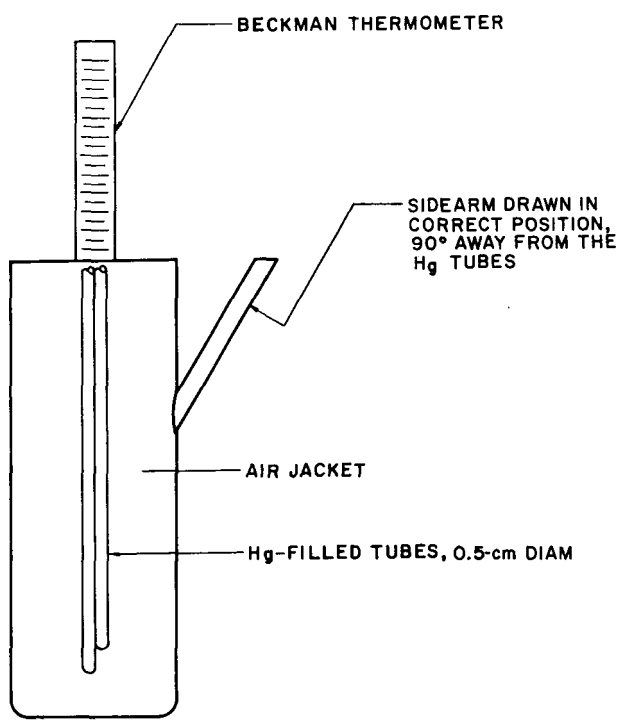



Fig. 7.
View 1 of conductivity cell.

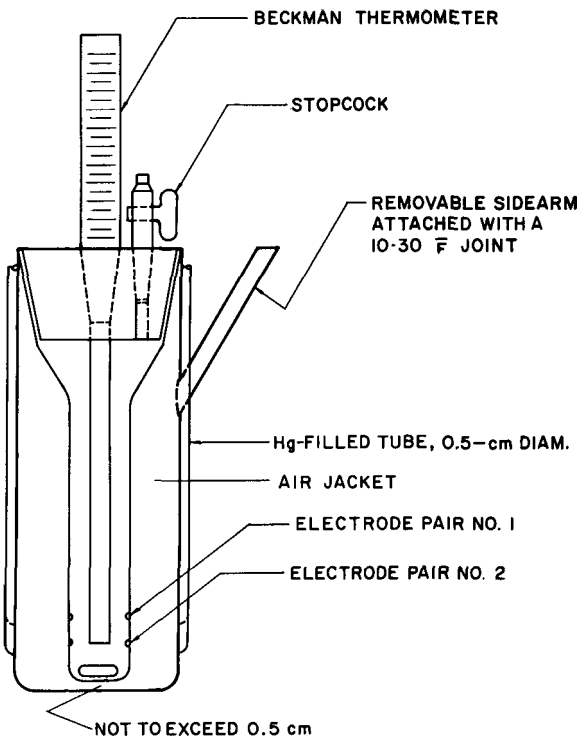



**Fig. 8.**
**View 2 of the conductivity cell.**

25°C). For the study of TNA, we used a cell constant (for the No. 1 electrodes) of 0.812 $cm^{-1}$. For the studies of TATB, TADNB, and TACDNB, we used a cell constant (for the No. 1 electrodes again) of 0.810 $cm^{-1}$.

An attempt was made to prepare 100% $H_2SO_4$ by adding $SO_3$ by drops to a glass container of 96-98% reagent-grade $H_2SO_4$ in a glove box flushed with dry nitrogen. The $SO_3$ was added in successive steps until the specific conductance and freezing point of the resulting liquid closely approximated that of 100% $H_2SO_4$ (L = 0.010439, fp = 10.365°C).[6]

By mixing the appropriate weighed amounts of solute and solvent, we made up solutions of TNA, TATB,* TADNB, and TACDNB in separate batches of 100% $H_2SO_4$ in a glove box flushed with dry nitrogen. We determined the freezing points of the solvent and solutions using the conductivity-cryoscopic cell fitted with a Beckmann thermometer. The closed cell was placed in a 4-6°C water bath, and the solvent or solution contained within the cell was super-cooled to 0.5-1.5° below its freezing point. After we inserted a platinum wire previously cooled in solid $CO_2$ into the super-cooled liquid to initiate solidification, we took the resulting freezing point.

A platinum resistance thermometer, calibrated by the National Bureau of Standards, was used to calibrate the Beckmann thermometer. We determined the true temperature using the following formula, $T_{true} = T_{Beckmann} + 6.214°C$. The resulting temperature had a standard deviation of 0.0092°C root.

We did not actually achieve 100% $H_2SO_4$ for our solvent using the freezing point of the solvent as our criterion (Table X). The impurity was probably either $H_2O$ (which would be protonated to give $H_3O^+$ and $HSO_4^-$) or $SO_3$ (which would react with $H_2SO_4$ to give $H_2S_2O_7$). Table X gives the freezing points of solutions of $H_3O^+$ $HSO_4^-$ and $H_2S_2O_7$ in 100% $H_2SO_4$ over the concentration range pertinent to our study.

To measure conductivity, we placed the closed cell in a mineral oil bath at 25.0°C and measured the resistance using the No. 1 electrodes (Fig. 8) in the cell. An ac Wheatstone bridge circuit, assembled from components available in the Laboratory, was used to measure the cell resistance. The components included a Leeds & Northrup Co. ac/dc decade resistor, an audio oscillator, standard resistors, a variable capacitor, and a pair of earphones and a Telequipment D66 oscilloscope as null detectors. With this circuit, we measured conductivity cell resistances with an absolute precision of 0.1 Ω and a relative precision range of 0.13-0.5%. The specific conductance of the solution in the cell, L, is equal to the cell constant (referred to above) divided by the measured resistance.

*Two different batches, a and b.

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