MASTER

CHEMICAL ANALYSIS OF TATB

B. D. Faubion

DEVELOPMENT DIVISION

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Mason & Hanger-Silas Mason Co., Inc.
Pantex Plant
P. O. BOX 647
AMARILLO, TEXAS 79177
806-335-1581

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ABSTRACT

The kinetics of the base hydrolysis of TATB has been studied as a function of hydroxide concentration and temperature. The initial rate of hydrolysis expressed as $k[\text{OH}^-]$ was determined by extrapolation to zero time. The values of the hydrolysis constant k determined at three temperatures were $3.24 \times 10^{-6} \text{ hr}^{-1}$ (50 C), $2.22 \times 10^{-5} \text{ hr}^{-1}$ (75 C) and $2.05 \times 10^{-4} \text{ hr}^{-1}$ (96 C).

An activation energy of $15 \pm 2 \text{ kcal mole}^{-1}$ was calculated from an Arrhenius plot. A method for analysis of the residue chloride in TATB is being developed utilizing base hydrolysis as a means of digesting the TATB and releasing the entrapped chloride. The chloride in the hydrolyzed solution is determined by potentiometric titration with standard silver nitrate using a specific ion electrode. The hydrolysis of 1,3,5-trichloro-2,4,6-trinitrobenzene (TCTNB) containing a small amount of 1,3-dinitro-2,4,6-trichlorobenzene (DNTCB) and 1,3-dinitro-2,4,5,6-tetrachlorobenzene (DNT₄CB) has also been studied to determine the amount of chloride released.

INTRODUCTION

A study of the hydrolysis of 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) is of interest for several reasons. This report is concerned with (1) the measurement of the rate of hydrolysis as a function of base concentration and temperature and (2) the development of a method for analysis of residue chloride by digesting the TATB in a strong alkaline solution. The base hydrolysis of TATB was reported in the literature(1).

Hydrolysis of all three amino groups gives a final product of 1,3,5-trihydroxy-2,4,6-trinitrobenzene (trinitrophloroglucinol). This material is also the final product of the hydrolysis of 1,3,5-trichloro-2,4,6-trinitrobenzene (TCTNB) and 1,3,5-trifluoro-2,4,6-trinitrobenzene (TFTNB)(2,3). Although it is assumed that the reaction occurs by the stepwise hydrolysis of the three amino groups in TATB or the three halogens in TCTNB or TFTNB, the mechanism has not been established.

Indeed the study of other related compounds (i.e., 2,4-dinitroaniline, picramide, and 1-chloro-2,4-dinitrobenzene) indicate that more than one interaction may be possible between these compounds and the base(4,5,6).

For the discussions in this report we will assume that the reaction of TATB with base occurs by the stepwise hydrolysis of the amino groups as given by Equation 1.

Although each step is actually reversible, the ammonia formed escapes and thus shifts the equilibria toward the right. For this reason the reverse reactions are not considered. If for a particular study there is a large excess of base, the OH^- concentration will be constant and can be incorporated in the rate constant (i.e., $k^* = k[\text{OH}^-]$). The rate equations for the three consecutive reactions can then be expressed as follows:

$$d[\text{TATB}]/dt = -k_1^* \quad (2)$$

$$d[\text{I}]/dt = k_1^* - k_2^* [\text{I}] \quad (3)$$

$$d[\text{II}]/dt = k_2^* [\text{I}] - k_3^* [\text{II}] \quad (4)$$

$$d[\text{III}]/dt = k_3^* [\text{II}] \quad (5)$$

The first reaction will be zero order with respect to the TATB since it is insoluble in the reaction medium. The rate constant k_1^* will therefore be dependent on the rate at which the following processes occur:

1. Diffusion of reactants to the surface.
2. Adsorption of reactants at the surface.
3. Chemical reaction on the surface.
4. Desorption of products.
5. Diffusion of products away from surface.

In order to test the validity of the proposed mechanism it will be necessary to isolate and identify the intermediate hydrolysis products and to establish values for the three rate constants. At the present time this phase of study is still in progress and in order to establish a method for predicting the stability of TATB toward hydrolysis a simplified rate expression was used.

An initial rate for the hydrolysis was determined by measuring the rate of formation of the hydrolysis product and extrapolating to time zero. This rate is useful for predicting the stability of the TATB toward hydrolysis, but does not reflect the mechanism by which the hydrolysis is occurring.

EXPERIMENTAL

To determine the rate of hydrolysis of the TATB, a weighed sample was placed in an excess of the base and the reaction vessel placed in a constant temperature bath. Aliquots of the reaction mixture were removed periodically, neutralized with acid and diluted to constant volume. The amount of hydrolyzed material was determined spectrophotometrically by measuring the absorbancy at 375 nm. The molar extinction coefficient of trinitrophenol was used to calculate the concentration. This value was determined experimentally to be 1.85×10^4 litre mole⁻¹ cm⁻¹ at 375 nm.

RESULTS AND DISCUSSION

The rate of hydrolysis of TATB was measured in five different concentrations of base at 50 C. The results are given in Table I. The initial rate for the 5 N NaOH is an order of magnitude greater than the other concentrations.

This may mean that a more complex interaction is occurring as suggested by Gold and Rochester(5).

The rate of hydrolysis was also measured at three temperatures for the 1 N NaOH. The results are given in Table II.

Table II. Hydrolysis of TATB in 1 N NaOH

<u>T (C)</u>	<u>Rate (hr⁻¹)</u>
50	3.24×10^{-6}
75	2.22×10^{-5}
96	2.05×10^{-4}

An Arrhenius plot for these values is shown in Fig. 1. The activation energy obtained from this plot is 15 ± 2 kcal mole⁻¹.

Table I. Rate of Hydrolysis of TATB at 50 C as a
Function of Base Concentration

$\frac{[\text{OH}^-]}{\text{Mole Litre}^{-1}}$	$\frac{\text{Rate}}{\text{Mole Litre}^{-1} \text{ hr}^{-1}}$	$\frac{\text{Rate}/[\text{OH}^-]}{\text{hr}^{-1}}$
5.00	2.16×10^{-4}	4.32×10^{-5}
1.00	3.24×10^{-6}	3.24×10^{-6}
0.50	1.30×10^{-6}	2.60×10^{-6}
0.10	3.24×10^{-7}	3.24×10^{-6}
0.05	1.62×10^{-7}	3.24×10^{-6}

Fig. 1. Arrhenius Plot for the Hydrolysis of TATB in 1 N NaOH

APPLICATION OF HYDROLYSIS TO CHLORIDE ANALYSIS OF TATB

One of the major drawbacks to the analysis of TATB is its extremely low solubility in most solvents.

For this reason the method that has been used for analysis of the residue chloride was based on the combustion of a sample in a Parr bomb followed by a determination of the chloride released during combustion and absorbed in the water in the bomb.

The residue chloride in the TATB is attributed to two sources—inorganic and organic. The inorganic chloride is thought primarily to be ammonium chloride, a by-product of the amination, which is entrapped in the TATB. The organic chlorides are thought to result from the partial amination of TCTNB, DNTCB, or DNT₄CB. By hydrolyzing the TATB in strong alkali the inorganic chlorides would be released. TCTNB will also be hydrolyzed in strong base releasing chloride ions but at a slower rate than TATB(1). A sample of TCTNB (Lot 4339-14-02) containing 9 percent DNT₄CB and 2.7% DNTCB was hydrolyzed using the conditions for TATB in order to determine if all of the chlorides are liberated. The results are given in Table III.

Table III. Hydrolysis of TCTNB with 3 N NaOH

<u>Time (hr)</u>	<u>% Cl⁻</u>	<u>Hydrolyzed (%)</u>
2	1.3	3.7
3	1.8	5.2
4	2.4	6.8
5	2.0	5.7
10	4.2	12.0
14	6.4	18.3
20	10.7	30.6
24	13.2	37.9

The percent of hydrolysis was calculated based on the total theoretical percent predicted for the composition of the mixture. These results indicate that under the conditions used for the chloride analysis of TATB (i.e., hydrolysis for three hours in 3 N NaOH) only about 5 percent of the organic chlorides are released. This number should be qualified, since the composition of the organic chlorides present in TATB is probably more complex than the sample tested. A better number could be obtained if a sufficient sample of the organic impurities could be obtained for analysis.

In view of these results, the amount of chloride analyzed by the hydrolysis method is probably something less than the total present in the sample, but greater than the inorganic chlorides only.

In order to establish a procedure for the chloride analysis by base hydrolysis of the TATB, several batches have been analyzed and the results compared with the Parr bomb results. The results are given in Table IV.

These results show that if the base concentration is too low or if the hydrolysis time is too short all of the TATB will not be hydrolyzed. Based on these results the following procedure for analysis is suggested:

1. Weigh accurately 1 g TATB into a 250 ml erlenmeyer flask.
2. Add 100 ml 3 N NaOH and heat to boiling on a steam bath for 3 hours.
3. Place the flask in a water bath to keep cool and neutralize with 5 N H_2SO_4 . The acid must be added slowly and with care to prevent sputtering.
4. Filter to remove trinitrophenol which may have precipitated.
5. Transfer the filtrate quantitatively to a 250 ml volumetric flask and dilute to volume.
6. Titrate a 50 ml aliquot of the solution with 0.05 N AgNO_3 using a Cl^- ion electrode and pH meter to determine the end point.
7. A blank should be run to correct for chloride impurities in the NaOH and H_2SO_4 .

FUTURE WORK

A more complete study of the hydrolysis of TATB will be conducted in order to establish the mechanism. Preliminary work using TLC indicates that the hydrolysis does indeed occur stepwise. It is hoped that liquid chromatography can be used to follow the formation and disappearance of each intermediate as a function of hydrolysis time.

Additional samples of TATB will be analyzed by the hydrolysis method and the results compared with the Parr method and other methods for chloride determinations.

Table IV. Chloride Analysis of TATB

<u>Sample</u>	<u>N NaOH</u>	<u>Time (hr)</u>	<u>Hydrolysis % Cl</u>	<u>Parr % Cl⁻</u>
4254-16-01	5	1	0.66	0.59
4267-16-01	5	1	0.93	0.85
4303-16-01	5	1	0.63	0.60
4304-16-01	5	1	0.71	0.60
4305-16-01	5	1	0.58	0.51
4283-16-01	1	4	4.02	4.64
4295-16-01	1	4	0.40	0.42
4291-16-02	2.5	1.5	0.54	0.55
4290-16-03	2.5	1.5	0.55	0.51
4267-16-01	2.5	1.5	0.84	0.85
4317-16-02	3	0.5	0.25	0.58
4317-16-02	3	1.0	0.58	0.58
4317-16-02	3	1.5	0.64	0.58
4317-16-02	3	2.0	0.69	0.58
4317-16-02	3	2.5	0.74	0.58
4317-16-02	3	3.0	0.89	0.58
4317-16-02	3	4.0	0.89	0.58
4317-16-02	3	5.0	0.90	0.58

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