27.ene
9/14/77
25 to NTIS

MASTER

UCID- 17542

Lawrence Livermore Laboratory

The Photometric Determination of 1,3,5-triamino-2,4,6-trinitrobenzene (TATB)
in Dimethylsulfoxide (DMSO).

Walter Selig

July 21, 1977

This is an informal report intended primarily for internal or limited external distribution. The opinions and conclusions stated are those of the author and may or may not be those of the laboratory.

Prepared for U.S. Energy Research & Development Administration under contract No. W-7405-Eng-48.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

The Photometric Determination of
1,3,5-triamino-2,4,6-trinitrobenzene (TATB)
in Dimethylsulfoxide (DMSO).

Walter Selig

ABSTRACT

NOTICE
This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

The molar absorbance, ϵ , of several lots of TATB in DMSO at 355 nm was measured. It ranged from 2.80×10^4 to 2.84×10^4 . Beer's law applies up to at least 0.36 mg of TATB/25 ml ($5.6 \times 10^{-5}M$). Attempts to enhance the sensitivity of the photometric method by using specific reagents for polynitroaromatic compounds have failed.

INTRODUCTION

We previously reported the estimated solubility of TATB in various solvents.¹ Of these solvents, DMSO is available in high purity and also has fair solvent power for TATB. DMSO has been used by MacDougall² in a liquid chromatographic assay of TATB. It is required for the determination of the DMSO-soluble content of TATB in the Material Specification for TATB by Los Alamos Scientific Laboratory.³ We have, therefore, determined the molar absorbance, ϵ , of several lots of TATB in DMSO at 355 nm. In addition, we attempted to increase ϵ for TATB by reaction with several reagents specific for polynitroaromatic compounds.

EXPERIMENTAL

Equipment and Materials

Beckman DK-2A ratio recording spectrophotometer with 1-cm silica cells.
Ultrasonic generator, Branson Instrument Company.
DMSO, "Baker Analyzed" reagent.
Ethylenediamine (EDA), Mallinckrodt Organic Reagent, 98%.
Tetraethylammonium hydroxide (TEAH), 10% aqueous, Eastman Organic Chemicals.

Determination of molar absorbance

Weigh between 2 and 3 mg of TATB on a microbalance and transfer to a 100-ml volumetric flask. Add approximately 90 ml of DMSO, stopper, and place into the tank of an ultrasonic generator for 30 min. at ambient temperature. Let the flask stand overnight and examine carefully for any undissolved TATB which may settle out. If necessary, repeat the ultrasonic treatment. Cool to ambient temperature and dilute to volume with DMSO. Take several aliquots (we found approximately 0.1 and 0.2 mg of TATB/25 ml satisfactory) and read or record the absorbance in a 1 cm cell vs. DMSO. Calculate ϵ from

$$\epsilon = \frac{A}{C}$$

Where A is the absorbance and C the concentration in moles/liter.

Reaction with Ethylenediamine (EDA)⁴

Place an aliquot containing approximately 0.2 mg of TATB in DMSO into a 25 ml volumetric flask. Dilute to volume with a 10% (v/v) solution of EDA/DMSO. Read the absorbances at 418 nm and 355 nm in a 1 cm silica cell vs. DMSO.

Reaction with Tetraethylammonium hydroxide (TEAH)^{5,6}

Transfer an aliquot containing approximately 0.2 mg of TATB in DMSO into a 25 ml volumetric flask. Add 1 ml of a 10% aqueous solution of TEAH and dilute to volume with DMSO. Read the absorbances at 438 nm and from 325-335 nm in a 1 cm silica cell vs. DMSO.

RESULTS AND DISCUSSION

Ungnade⁷ determined the absorption spectrum of TATB in concentrated sulfuric acid in the ultraviolet range. At 272 nm the molar absorbance was 1.29×10^4 and at 324 nm it was 2.545×10^4 (note the accidental reversal of the figures in the original report). We have used the approximate value of 2.5×10^4 for ϵ in order to estimate the solubility of TATB in various solvents.¹ In most

organic solvents the absorption maximum occurred near 355 nm while in acidic solvents such as sulfuric acid TATB exhibits a hypsochromic shift.

DMSO ranks high in its solvent power for TATB. It is exceeded only by methanesulfonic acid, hexamethylphosphortriamide, and ethanesulfonic acid. It is available in high purity and is less expensive than the three higher ranking solvents. It is used in the determination of the DMSO-soluble content of TATB according to the Los Alamos Scientific Laboratory Materials Specification for TATB³ and in a chromatographic method for TATB.² We have, therefore, determined ϵ of various lots of TATB in DMSO. The results are shown in Table 1. The standard deviations are based on duplicate scans of each sample as well as a minimum of two samples containing different amounts of TATB. ϵ for the various lots of TATB ranged from 2.80 to 2.84×10^4 . It is noteworthy that double extraction with acetone did not change ϵ appreciably. Lot B-437 is one with extremely low chlorine content (total Cl 0.03%) and of fairly large particle size. This particular lot required 1 hour of ultrasonic agitation in order to dissolve the entire amount (≈ 2 mg/100 ml) of TATB.

A calibration curve for Lot B-377 is shown in Figure 1. Beer's law applied up to at least 0.36 mg of TATB/25 ml DMSO (5.6×10^{-5} M). At the highest concentration of TATB the absorbance was approximately 1.6.

The precision of ϵ is limited by our ability to measure absorbances accurately. The smallest scale unit is 0.01 and we believe it possible to estimate absorbances to ± 0.002 units. At the 0.1 mg/25 ml level the uncertainty of ϵ therefore is $\pm 0.013 \times 10^4$, at the 0.2 mg/25 ml level it is $\pm 0.006 \times 10^4$.

MacDougall² reported a value of 2.58×10^4 for the molar absorbance of TATB in DMSO. We find this value to be rather low. Her chromatographic procedure requires warming 10 mg of TATB in 100 ml DMSO until it is dissolved. On cooling, a supersaturated solution may result. Based on our experience it is difficult to dissolve more than 5 mg of TATB/100 ml DMSO at ambient temperature. We avoid heating solutions to increase the solubility of TATB because the effect of heating on TATB and the possible molecular interactions are not presently known.

Sawicki and Stanley⁵ reported the detection and determination of polynitro-aromatic compounds with TEAH. The writer modified this method for the photometric determination of some nitro derivatives of diphenylamine in N,N-dimethylformamide (DMF).⁶ We have used this method for TATB in DMSO (rather than DMF). An absorption

peak was found at 438 nm ($\epsilon = 1.49 \times 10^4$) and a rather broad band from 325 to 335 nm ($\epsilon = 1.97 \times 10^4$). These molar absorbances are less than in DMSO alone and thus afford no improvement.

We previously reported the apparent solubility of TATB in EDA as 2195 ppm, based on the λ_{max} at 408-410 nm. We assumed this absorption to be due to possible hydrolysis of the amine moiety. Based on an infrared analysis of the residue, it seems more likely that this peak is caused by partial replacement of an amine hydrogen by EDA. Glover and Kayser have used a similar reaction for the photometric determination of polynitroaromatic compounds. When their method was applied to TATB a λ_{max} was found at 418 nm ($\epsilon = 1.53 \times 10^4$) while the 355 nm peak was preserved, although at lower intensity than in DMSO alone ($\epsilon = 1.72 \times 10^4$). Increasing the EDA concentration did not affect the 418 nm peak while slightly decreasing the 355 nm peak. Thus, this method also did not yield an increase in ϵ for TATB.

Because of the narrow range found in molar absorbance for several lots of TATB in DMSO, we recommend that this method be considered as a quality control method for TATB.

REFERENCES

1. W. Selig, "How to Estimate the Solubility of an Insoluble Compound - TATB," Lawrence Livermore Laboratory Rept. UCID-17412, Rev. I (April 1977).
2. C. S. MacDougall, "A Liquid Chromatographic-Spectrophotometric Assay for TATB in TATB," in Quarterly Progress Report, January-March 1977, Rept. MHSMP-77-18.
3. "Material Specification for TATB," Los Alamos Scientific Laboratory drawing 13Y-188025, Rev. B, released April 25, 1977.
4. D. J. Glover and E. G. Kayser, Anal. Chem. 40, 2050 (1968).
5. E. Sawicki and T. W. Stanley, Analyt. Chim. Acta, 23, 551 (1960).
6. W. Selig, "The Spectrophotometric Determination of Some Nitro and Nitroso Derivatives of Diphenylamine in N,N-Dimethylformamide," Lawrence Livermore Laboratory Rept., UCRL-6903 (May 8, 1963).
7. H. E. Ungnade, "1,3,5-Triamino-2,4,6-Trinitrobenzene (TATB) - Preparation and Purification," Los Alamos Scientific Laboratory, Rept., GMX-2-R-64-1 p. 10-11, (1963).

TABLE 1

Molar Absorbance of Various Lots of TATB at 355 nm in DMSO

Lot No.	Treatment	$\epsilon \times 10^{-4}$	Std. Dev.	Number of replicates
B-377	as received	2.83	0.027	11
B-338	as received	2.80		
B-388	2 X acetone extracted	2.81	0.008	4
B-317	as received	2.84	0.007	4
B-317	2 X acetone extracted	2.81	0.005	4
B-437	as received	2.81	0.005	4
B-456	as received	2.80	0.004	4
B-456	2 X acetone extracted	2.80	0.004	4
B-457	as received	2.80	0.004	4
Reference 7 (sulfuric acid)		2.545		
Reference 2		2.58		

FIGURE 1: ABSORBANCE VS. CONCENTRATION FOR TATB LOT B-377.

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research & Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately-owned rights.

NOTICE

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Energy Research & Development Administration to the exclusion of others that may be suitable.

Printed in the United States of America
Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161
Price: Printed Copy \$; Microfiche \$3.00

Page Range	Domestic Price	Page Range	Domestic Price
001-025	\$ 3.50	326-350	10.00
026-050	4.00	351-375	10.50
051-075	4.50	376-400	10.75
076-100	5.00	401-425	11.00
101-125	5.50	426-450	11.75
126-150	6.00	451-475	12.00
151-175	6.75	476-500	12.50
176-200	7.50	501-525	12.75
201-225	7.75	526-550	13.00
226-250	8.00	551-575	13.50
251-275	9.00	576-600	13.75
276-300	9.25	601-up	*
301-325	9.75		

* Add \$2.50 for each additional 100 page increment from 601 to 1,000 pages; add \$4.50 for each additional 100 page increment over 1,000 pages.

Technical Information Department

LAWRENCE LIVERMORE LABORATORY

University of California | Livermore, California | 94550