

[CONTRIBUTION FROM THE EXPLOSIVES LABORATORY, CHEMICAL DIVISION, PITTSBURGH EXPERIMENT STATION, UNITED STATES BUREAU OF MINES]

THE SOLUBILITY OF TETRANITRO-ANILINE IN ORGANIC SOLVENTS¹

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The solubilities of trinitrotoluene⁴ and of trinitro-phenylmethyl-nitramine (tetryl)⁵ in various solvents have already been determined in this Laboratory at the suggestion of Dr. C. E. Munroe, Chairman of the Committee of Explosives Investigation of the National Research Council, and it was in continuation of this work that it was decided to determine the solubility of tetranitro-aniline, "T. N. A.," in various solvents.

Because of the instability of the *m*-nitro group of this compound in the presence of moisture, it was anticipated that difficulty might be encountered in the course of this work. Accordingly, every precaution was taken to avoid this hydrolysis; but it was found that when tetranitro-aniline was subjected to any considerable temperature change, particularly a heating and subsequent cooling, decomposition took place to a considerable extent, even in anhydrous solvents and the results obtained were of little value. It was then decided to make determinations at 0.0° only, so that this source of error might be eliminated as much as possible.

Materials.—The tetranitro-aniline used in the following determinations was a fine, crystalline product of a chrome-yellow color. This product was obtained by dissolving high-grade commercial "T. N. A." of a greenish tint in warm (not boiling), anhydrous, c. p. acetone, filtering to remove any insoluble matter, and allowing the clear solution to cool to room temperature. Evaporation was not resorted to, only the precipitated solid being filtered off for use. This was quickly washed with a little cold acetone and pressed between filter paper. The residual acetone was removed by evaporation with dried air, and the yellow, finely powdered mass was then placed in a sulfuric acid desiccator in a dark place, where it was allowed to remain for a month before use. When slowly heated in an air-jacketed tube, it began to darken at 200°. At 215° to 217° it became black and began to liberate gas. This decomposition is strongly exothermic, the temperature rising rapidly to 225°, and at this temperature there is usually violent combustion.

Solvents.—The solvents used in this work were the same lots of purified

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⁴ Taylor and Rinkenbach, *THIS JOURNAL*, **45**, 44 (1923).

⁵ Taylor and Rinkenbach, *ibid.*, **45**, 104 (1923).

solvents used in the study of the solubility of trinitrotoluene⁴ with the exception of methanol and ethanol, which were absolute.

Method

The method was that of obtaining solutions in equilibrium with an excess of the solute at a definite temperature, removing samples by means of the wagon-pipet,⁴ weighing, evaporating the solvent, and reweighing the dry tetranitro-aniline.

The solvent and solute were placed in a glass tube which was tightly stoppered, and almost complete saturation at room temperature was brought about by shaking the mixture for several hours.* The tube and contents were then immersed in a large, well insulated ice-bath, which soon lowered the temperature to within 0.1° of 0.0°. After being maintained at this temperature for 24 to 48 hours, a sample of 100 to 300 g. of the solution was drawn through a cotton plug filter into an evacuated wagon-pipet. After coming to room temperature, the sample was weighed and then transferred to a dried, weighed beaker. This was loosely covered to keep out dust, and the solution was allowed to evaporate spontaneously at room temperature. When all of the solvent had been evaporated, the beaker and residue were dried for 1 hour at 60° and placed in a desiccator for 2 hours before weighing in order to determine the solid residue. The result so obtained was calculated to the basis of grams of solute per 100 g. of solvent.

It was impossible to follow this exact procedure with benzene. Benzene freezes at about 5° and the addition of tetranitro-aniline lowered the freezing point to 3.9°. Accordingly, after saturation of the solvent at air temperature, the tube containing the solution and the excess of solute was air-jacketed and immersed in the ice-bath. The mixture was stirred continuously. Freezing began at 3.9° and the temperature remained constant. A sample was withdrawn by means of a wagon-pipet and the subsequent procedure was identical with that given for the determinations with other solvents. Triplicate determinations were made in all cases.

TABLE I
SOLUBILITIES OF TETRANITRO-ANILINE

	Grams per 100 g. of solvent			Av.
	1	2	3	
Water.....	0.0064	0.0081	0.0069	0.007
Methyl alcohol.....	0.448	0.476	0.437	0.45
Ethyl alcohol.....	0.323	0.344	0.352	0.34
Ether.....	0.0813	0.0808	0.0809	0.081
Acetone.....	7.59	7.42	7.49	7.50
Chloroform.....	0.0110	0.0096	0.0106	0.010
Carbon tetrachloride.....	0.0029	0.0038	0.0040	0.0036
Carbon disulfide.....	0.0054	0.0058	0.0056	0.0056
Benzene (3.9°).....	0.148	0.133	0.119	0.13
Toluene.....	0.1895	0.1891	0.1861	0.188

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Summary

It was found impracticable to determine accurately the solubility of tetranitro-aniline in the various solvents at room temperature or higher temperatures because of the tendency of the solute to decompose while in solution, so determinations were made at 0.0° except with benzene with which solubility was determined at the freezing point of 3.9°.

The solubility of tetranitro-aniline in these solvents is slightly lower than that of tetryl under the same conditions.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

A PRECISION MEASUREMENT OF THE COMPOSITION OF THE CONSTANT-BOILING MIXTURE OF HYDROGEN CHLORIDE AND WATER

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This paper offers a series of precision measurements of the composition of the constant-boiling mixture of hydrogen chloride and water as it is prepared for use in acidimetry. It is one of a series from the Ohio State Laboratory in which atomic-weight methods have been employed in studying substances used as standards in chemical measurements.

The importance of this constant-boiling mixture in volumetric analysis is sufficient warrant for such a precision study, but in addition there is the gratification of scientific curiosity as to whether the peculiar balance of physical conditions which arises in the distillation of the acid and water will produce a mixture which in definiteness of composition approaches a true chemical compound.

Historical

The existence of a constant-boiling mixture of hydrogen chloride and water has been known since the days of Dalton. Bineau¹ and Roscoe and Dittmar² published papers on it but Hulett and Bonner³ were the first to suggest its use as a standard in volumetric analysis and to offer determinations of its composition that could be accepted by analytical chemists. The following quotation describes their procedure for obtaining a mixture of constant composition. "By starting with hydrochloric acid about $d. = 1.10$, made up with an ordinary hydrometer or sp. gr. balance, and distilling off $\frac{3}{4}$ of the liquid taken, the following distillate should not differ by more than one part in 10,000 from the

¹ Bineau, *Ann. chim. phys.*, [3] **7**, 257 (1843).

² Roscoe and Dittmar, *J. Chem. Soc.*, **12**, 136 (1860).

³ Hulett and Bonner, *THIS JOURNAL*, **31**, 390 (1909).