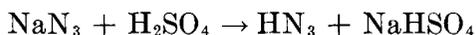


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26. HYDROGEN AZIDE IN AQUEOUS AND ETHEREAL SOLUTIONS



SUBMITTED BY L. F. AUDRIETH* AND C. F. GIBBS*

CHECKED BY W. C. JOHNSON† AND H. C. PERRIN‡

Aqueous solutions of hydrogen azide are readily obtained by treatment of sodium azide‡ with sulfuric acid. Since pure hydrogen azide is **extremely explosive**, and since its vapors produce most unpleasant physiological effects, it is advisable to use care in its preparation. Especially is the treatment of dry sodium azide, or of a cold solution, with sulfuric acid to be avoided, since this results in the formation of pure hydrogen azide (b. 37°C.) which may condense to the anhydrous liquid or to a highly concentrated aqueous solution, both of which are extremely explosive.

In addition to the method outlined under procedure A, hydrazoic acid may be prepared by the action of oxalic¹ or fluosilicic acids² upon solutions of sodium azide or by the treatment of barium azide solutions with dilute sulfuric acid. A method involving the action of perchloric acid upon potassium azide has also been proposed. However, subsequent distillation of the filtrate, after removal of the precipitated potassium perchlorate, is necessary to prepare pure hydrazoic acid. Pure hydrazoic acid has also been obtained by the oxidation of hydrazine in acid solution by hydrogen peroxide.³⁻⁵

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Procedure

A. HYDRAZOIC ACID (AQUEOUS SOLUTION OF HYDROGEN AZIDE)

Fifteen grams of sodium azide and 5 g. of sodium hydroxide* are dissolved in 150 ml. of water contained in a 250-ml. distilling flask fitted with a dropping funnel and attached to an efficient condenser. The end of the condenser is connected by means of an adapter to a 500-ml. filter flask containing 100 ml. of water. A tube leading to a hood outlet is connected to the side arm of the filter flask. The solution in the distilling flask is brought to the boiling point (**very important!**), and 90 ml. of 40 per cent sulfuric acid is then added drop by drop. The distillation is continued until only about 50 ml. of solution remains in the distilling flask. Hydrazoic acid containing about 3 per cent of hydrogen azide (0.6 to 0.7N) may be obtained in this way.

B. ANHYDROUS ETHEREAL SOLUTION OF HYDROGEN AZIDE

Since the distribution ratio of hydrogen azide between the two solvents ether and water is approximately 7:1, ethereal solutions may be prepared by extraction of aqueous solutions with ether. However, the procedure used by Frost, Cothran, and Browne⁶ is preferable.

Thirty grams of sodium azide, dissolved in 100 ml. of water and 150 ml. of ether, is placed in a 500-ml. round-bottom flask. The latter is connected through a Hopkins (or Reitmeier) bulb with a suitable condenser and a receiving vessel. The receiver contains 100 ml. of ether and is immersed in an ice bath. The generator is also fitted with a dropping funnel which dips below the surface of the solution and through which 30 ml. of concentrated sulfuric acid is slowly introduced. Most of the hydrogen azide and ether distill into the receiver during the addition

* The addition of sodium hydroxide is purely precautionary. It avoids the formation of a high concentration of hydrogen azide in a cold solution.

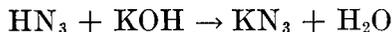
of the acid. The remainder may be recovered by heating the flask on a steam bath for a short time. The ethereal distillate is dried over calcium chloride and then redistilled from the desiccant.

References

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2. HOTH and PYL: *Z. angew. Chem.*, **42**, 888 (1929).
3. BROWNE: *J. Am. Chem. Soc.*, **27**, 551 (1905).
4. MARTIN: *J. Am. Chem. Soc.*, **49**, 2133 (1927).
5. AUDRIETH: *Chem. Rev.*, **15**, 169 (1934).
6. FROST, COTHRAN, and BROWNE: *J. Am. Chem. Soc.*, **55**, 3516 (1933).

27. POTASSIUM AZIDE*

(Alkali and Alkaline Earth Azides)



SUBMITTED BY A. W. BROWNE†

CHECKED BY L. F. AUDRIETH† AND E. LANNERUD‡

Potassium, rubidium, and cesium azides are of particular interest, since they undergo thermal decomposition at higher temperatures with the formation of the free alkali metals and the evolution of nitrogen in accordance with the equation



These azides may therefore be employed for the preparation of small quantities of very pure potassium, rubidium, or cesium.¹ They have also been decomposed to obtain very pure nitrogen.²

Only the preparation of potassium azide is described here. However, the method outlined below can be adapted to the preparation of the alkali and alkaline earth azides in general. It is also suggested for the purification of technical sodium azide. The usual methods for the synthesis of sodium azide by the nitrous oxide-sodium amide³ method or the hydrazine-alkyl nitrite⁴ procedure have either not

* Azides are also called trinitrides, azoimides, and triazoates.

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yet been or are not easily adapted to the direct preparation of the other azides. Consequently, technical sodium azide⁵ must serve as the starting material for their preparation.

Procedure

A 3 per cent solution of hydrazoic acid (synthesis 26A) is neutralized with an aqueous solution of pure potassium hydroxide. The resulting solution of potassium azide is concentrated on the steam bath to incipient crystallization. The solution is then made slightly acid with hydrazoic acid to replace the hydrogen azide lost by hydrolysis. A volume of ethyl alcohol twice that of the solution is added, and the solution is cooled in an ice bath. Since the solubility in alcohol of the alkali and alkaline earth azides is very slight (see table below), precipitation in the form of a white microcrystalline salt takes place readily. From 90 to 95 per cent recovery of the theoretical quantity of potassium azide can be effected. The precipitated azide is filtered on a Büchner funnel and washed with cold absolute alcohol and then with ether. Any traces of adhering solvent may be removed in a vacuum desiccator. In a typical run, 300 ml. of a solution of hydrazoic acid containing 8.5 g. of HN_3 was neutralized with potassium hydroxide, and the isolation of potassium azide effected as indicated above. Yield 14.7 g. (91.5 per cent) KN_3 .

Properties⁶

The melting points of those azides which melt without decomposition are given in the first column of the table below. The decomposition temperatures noted in the second column are those determined by Tiede⁷ and by Suhrmann and Clusius¹ and refer to the temperatures at which decomposition of the azides into metal and nitrogen takes place. Once such decomposition has begun, it may be continued at a lower temperature, as indicated by the figures given in the third column. The solubilities of the azides in water and in ethyl alcohol are also summarized.

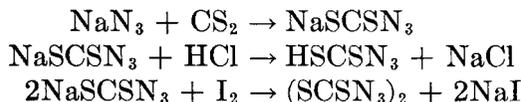
PROPERTIES OF THE ALKALI AND ALKALINE-EARTH AZIDES⁶

Formula	M., °C.	Initial decomposition temp., °C.	Decomposition temp., °C.	Solubility in 100 g. H ₂ O, g.	Solubility in 100 g. C ₂ H ₅ OH, g.
LiN ₃	66.41 16°	20.26 16°
NaN ₃	300	280	41.7 17°	0.22 0°
KN ₃	350	355	360	49.6 17°	0.14 16°
RbN ₃	330	395	310	114.1 17°	
CsN ₃	326	390	350	307.4 16°	1.04 16°
Ca(N ₃) ₂	110	100	45. 15.2°	0.211
Sr(N ₃) ₂	140	110	45.83 16°	sl. sol.
Ba(N ₃) ₂	160	120	16.7 15°	sl. sol.

References

1. SUHRMANN and CLUSIUS: *Z. anorg. allgem. Chem.*, **152**, 52 (1926).
2. JUSTI: *Ann. Physik*, [5] **10**, 983 (1931).
3. DENNIS and BROWNE: *J. Am. Chem. Soc.*, **26**, 577 (1904).
4. THIELE: *Ber.*, **41**, 2681 (1908); STOLLÉ: *Ber.*, **41**, 2811 (1908); WILCOXON and GROTTA: U. S. patent 1,628,380.
5. Eastman Kodak Company, Rochester, N. Y.
6. For a comprehensive discussion of hydrazoic acid and its inorganic derivatives, see AUDRIETH: *Chem. Rev.*, **15**, 169 (1934).
7. TIEDE: *Ber.*, **49**, 1742 (1916).
8. This is from a more complete table given by AUDRIETH (see ref. 6, p. 203).

28. AZIDODITHIOCARBONIC ACID (AZIDOTHIOFORMIC ACID) AND AZIDOCARBONDISULFIDE



SUBMITTED BY G. B. L. SMITH*
CHECKED BY FRANK WILCOXON†

A few salts of azidodithiocarbonic acid were first prepared by Sommer¹ by the reaction of azides (trinitrides) with carbon disulfide:

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