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ANHYDROUS HYDRAZINE. V. HYDRAZINATES OF CALCIUM TRINITRIDE^{1,2}

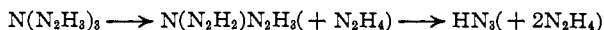
By A. L. DRESSER AND A. W. BROWNE

WITH MICROSCOPICAL STUDIES BY C. W. MASON

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It was first suggested by Frank Wilcoxon,³ in this Laboratory, that hydronitric acid may be regarded as a nitrous acid of the hydrazine system of compounds, theoretically derivable from the normal hydrazonitrous acid by dehydrazination in two stages, as follows



From this viewpoint hydronitric acid may be thought of as *metahydrazonitrous acid*, while hydrazine trinitride, $\text{N}_2\text{H}_5\text{N}_3$, empirically isomeric with *orthohydrazonitrous acid*, $\text{HN}(\text{NH}_2)\text{N}=\text{NNH}_2$, may possibly be identical with this acid. This compound is furthermore recognizable as *pentazene-2*, a hypothetical member of the diazene series of unsaturated hydronitrogens. Or, hydrazine trinitride might be identical with the structural isomer of this substance, *pentazene-1*, $\text{HN}=\text{NNHNHNH}_2$, which, although probably capable of forming metallic derivatives, cannot be formulated as one of the hydrazonitrous acids.

The monohydrinate of hydrazine trinitride, $\text{N}_2\text{H}_5\text{N}_3 \cdot \text{N}_2\text{H}_4$, first prepared in this Laboratory by H. E. Riegger,⁴ is, moreover, isomeric and possibly identical with *normal hydrazonitrous acid*, $\text{N}(\text{N}_2\text{H}_3)_3$, one of the

¹ For the earlier articles of this series see (a) Hale and Shetterly, *THIS JOURNAL*, 33, 1071 (1911); (b) Welsh, *ibid.*, 37, 497 (1915); (c) Welsh and Broderson, *ibid.*, 37, 816 (1915); (d) Welsh and Broderson, *ibid.*, 37, 825 (1915).

² The investigation upon which this article is based was supported by a grant from the Heckscher Foundation for the Advancement of Research, established by August Heckscher at Cornell University. The present paper is Article No. 1 under Heckscher Grant No. 158. For references to earlier articles published under Heckscher Grants No. 4 and No. 60, see *THIS JOURNAL*, 52, 2799 (1930), footnote 1; 52, 2806 (1930), footnote 2.

³ Browne and Wilcoxon, *ibid.*, 48, 682 (1926).

⁴ Ref. 3, footnote 13.

heptazanes, which are higher homologs of the ammonia (*monazane*) series of saturated hydronitrogens.⁵

On the assumption that progressive hydrazination of hydronitric acid yields these ortho and normal acids, or other higher hydronitrogens, it seems reasonable to suppose that similar treatment of certain metallic trinitrides should yield hydrazinates that might be formulated as metallic salts of these or kindred acids. The present investigation has been undertaken for the purpose of testing this supposition for the case of the hitherto unknown hydrazinates⁶ of calcium trinitride.

Materials Used.—Calcium trinitride was prepared by acidifying a heavy suspension of calcium hydroxide in water with hydronitric acid according to the method of Dennis and Benedict.⁷ The resulting solution was concentrated by boiling, and was again acidified with a strong solution of the acid. Precipitation of the calcium trinitride was effected by the addition of a relatively large volume of acetone containing sufficient alcohol to insure miscibility of the liquids. The solid product was dried at room temperature over sulfuric acid.

Anhydrous hydrazine was prepared by dehydration of hydrazine hydrate with barium oxide in the manner described by Hale and Shetterly.^{1a} Analysis of the product by titration in moderately concentrated hydrochloric acid solution with standard potassium bromate by the method of Kolthoff⁸ showed a purity of 99.6%.

Calcium Trinitride Dihydrizate, $\text{Ca}(\text{N}_3)_2 \cdot 2\text{N}_2\text{H}_4$

Preparation.—A nearly saturated solution of calcium trinitride in anhydrous hydrazine was either (1) evaporated to dryness at room temperature over sulfuric acid in a vacuum desiccator, or (2) treated with absolute alcohol. The white, crystalline solid obtained by either procedure was dried to constant weight over sulfuric acid in an atmosphere of nitrogen gas.

Analysis.—(a) Hydrazine was determined by the Kolthoff method;⁸ (b) calcium, by precipitation as the oxalate and titration with potassium permanganate; (c) hydronitric acid, by the method of West.⁹

Anal. (a) Subs., 0.0942, 0.1234. Calcd. for $\text{Ca}(\text{N}_3)_2 \cdot 2\text{N}_2\text{H}_4$: N_2H_4 , 34.05. Found:

⁵ The results obtained by Doctor Riegger have been entirely confirmed during a later and more extended investigation of this compound, soon to be published.

⁶ Numerous hydrazinates of metallic salts have been described by other investigators. The following compounds of calcium salts with hydrazine, for example, have been described by Franzen and von Mayer [*Z. anorg. Chem.*, **60**, 247 (1908)]: $\text{Ca}(\text{NO}_3)_2 \cdot 2\text{N}_2\text{H}_4$, $\text{CaCl}_2 \cdot 2\text{N}_2\text{H}_4$, and $\text{CaBr}_2 \cdot 3\text{N}_2\text{H}_4$. So far as the authors are aware, however, no hydrazinates of the metallic trinitrides have as yet been described.

⁷ Dennis and Benedict, *THIS JOURNAL*, **20**, 225 (1898).

⁸ Kolthoff, *ibid.*, **46**, 2009 (1924).

⁹ West, *J. Chem. Soc.*, **77**, 705 (1900).

34.04, 34.15. (b) Subs., 0.2783, 0.2757. Calcd. for $\text{Ca}(\text{N}_3)_2 \cdot 2\text{N}_2\text{H}_4$: Ca, 21.29. Found: 21.39, 21.26. (c) Subs., 0.2547, 0.3445. Calcd. for $\text{Ca}(\text{N}_3)_2 \cdot 2\text{N}_2\text{H}_4$: N₃, 44.66. Found: 44.85, 44.86.

Properties.—Calcium trinitride dihydrazinate is a white, crystalline solid, extremely soluble in water. At 23°, 100 g. of solvent will dissolve the following weights of the compound: anhydrous hydrazine, 34.7 g.; methanol, 7 g.; ethanol, 0.4 g. It is not appreciably soluble in carbon tetrachloride, chloroform, benzene, acetone, diethyl ether, ethyl acetate, or carbon disulfide.

In the open air the dihydrazinate undergoes, at room temperature, a very slow spontaneous decomposition, with gradual loss of weight, due in part to efflorescence and in part to oxidation. Heated in a slow current of nitrogen to 57° for two hours, a small sample showed scarcely appreciable dehydrazination. After five hours at 95°, however, a loss in weight corresponding to one molecular equivalent of hydrazine was experienced. Further heating at this temperature showed a greatly retarded rate of loss, indicating the possible existence of a lower hydrazinate. Spread upon a modified Maquenne block,¹⁰ the dihydrazinate decomposes immediately with explosive violence at about 335°, and less rapidly at lower temperatures.

Under the microscope, calcium trinitride dihydrazinate crystallized from anhydrous hydrazine by evaporation *in vacuo*, yields crystals most commonly of rectangular tabular habit. These crystals belong to the orthorhombic system; if the crystallographic axes are located so that the flattening is parallel to *a* and *b*, the largest faces may be designated 100, and these are beveled by 110 and 101; the corners of the tablets are truncated by 011, and in some of the crystals these latter faces are of such size that 101 is absent, and the crystals are six-sided in outline, with terminal angles of about 70°.

All these principal views of the crystals exhibit parallel extinction, and biaxial interference figures may be obtained from crystals on end. $2V$ is about 80°, with $r > v$ distinct, and positive optical character. The axial plane is 100; the optic normal is *a*, and *c* is the acute bisectrix. $\gamma = 1.70$; $\beta = 1.610$; $\alpha = 1.583$, all ± 0.005 .

Structure.—As attested by the procedure adopted in the analysis of the dihydrazinate, this compound tends to hydrolyze and dissociate in aqueous solution, yielding the following ionic species: Ca^{++} , N_2H_5^+ , OH^- and N_3^- . Neither this fact nor the tendency of the dihydrazinate to lose hydrazine slowly when heated can fairly be considered to preclude the assumption of a chain structure of the pentazene type for this compound. While no organic compounds containing either a pentazane, a pentazene-1, or a pentazene-2 chain of nitrogen atoms seem as yet to have been isolated.

¹⁰ Dennis and Shelton, *THIS JOURNAL*, 52, 3128 (1930).

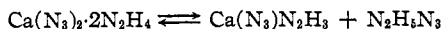
numerous derivatives of pentazdiene-1,4, known as the bisdiazamino compounds, have been prepared.¹¹

Compounds containing chains of more than two nitrogen atoms should naturally be expected for several reasons to break up or "crack" when subjected to heat, or to ionize, under suitable conditions, far more readily than chains of carbon atoms, yielding in similar fashion lower homologs or their derivatives. Phenylhippuryl buzylene, for example, a derivative of tetrazene-1, has been shown by Curtius¹² to decompose readily, yielding either hippuryl trinitride and aniline, or hippuryl amide and phenyl trinitride. The tetraalkyl derivatives of tetrazene-2 decompose with formation of nitrogen gas and derivatives of hydrazine.¹³

By reason of the foregoing facts the authors feel justified in presenting, as a tentative hypothesis, their opinion that calcium trinitride dihydrazinate may be formulated structurally either as a calcium orthohydrazonitrite, the calcium derivative of pentazene-2, or as the calcium derivative of pentazene-1. In view of the tendency of calcium to form coördination compounds, it may be possible that the terminal nitrogens of the pentazene-1 groups form coördinate linkages with the calcium atom, to produce a spiro structure of two six-membered rings.¹⁴ Until further experimental evidence is available, however, no definite conclusions can be reached concerning the structure of this compound.

Calcium Trinitride Monohydrazinate, $\text{Ca}(\text{N}_3)_2 \cdot \text{N}_2\text{H}_4$

Preparation and Properties.—Dehydrazination of the dihydrazinate of calcium trinitride in a current of nitrogen takes place in two fairly distinct stages. Repeated attempts to prepare satisfactory samples of the monosolvate by fractional dehydrazination, however, failed to yield altogether conclusive results, presumably owing to one or more of the following possible causes: (1) slight concurrent dehydrazination of the lower solvate; (2) partial hydrazinolysis of the calcium trinitride with formation of an hydrazobasic salt as expressed by the equation

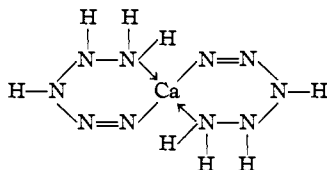


¹¹ See, for example, Griess, *Ann.*, **137**, 39 (1866); Goldschmidt and Holm, *Ber.*, **21**, 1016 (1888); Goldschmidt and Badl, *ibid.*, **22**, 933 (1889); v. Pechmann and Frobenius, *ibid.*, **27**, 703, 898 (1894); **28**, 170 (1895); Bamberger, *ibid.*, **29**, 446 (1896); Hantzsch, *ibid.*, **31**, 340 (1898); Dimroth, *ibid.*, **38**, 2328 (1905).

¹² Curtius, *Ber.*, **29**, 759 (1896).

¹³ Wieland, *Ann.*, **392**, 127 (1912).

¹⁴ This possible structure was suggested to the authors by Doctor John R. Johnson, Professor of Organic Chemistry at Cornell University.



and (3) thermal decomposition of the calcium trinitride¹⁵ with liberation of molecular nitrogen.

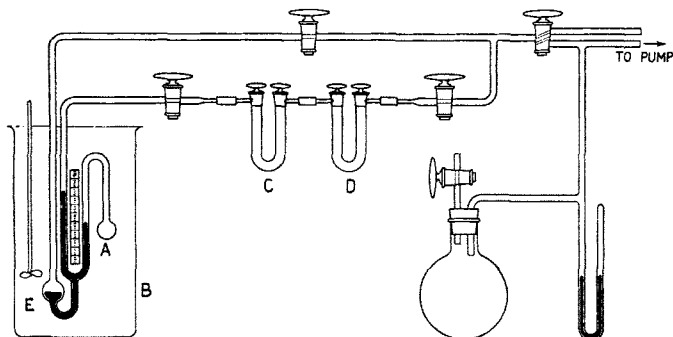


Fig. 1.—Apparatus for determining pressure-concentration isotherms.

That the difficulty is chiefly if not wholly attributable to the first of these possible causes is indicated by the absence of detectable amounts

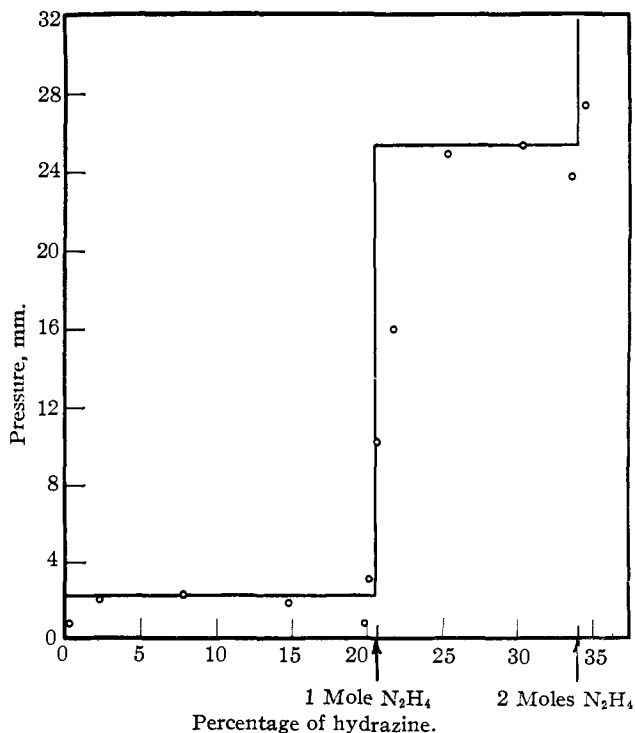


Fig. 2.—Pressure-concentration isotherm (100°) for the system calcium trinitride-hydrazine.

¹⁵ Tiede, *Ber.*, **49**, 1742 (1916).

of the volatile hydrazine trinitride, and by the absence of significant volumes of nitrogen gas from the products pumped from samples held at 100° or higher temperatures.

In order to secure evidence concerning the possible existence of the monohydrinate a pressure-concentration isotherm for the system calcium trinitride-hydrazine was determined at 100° with the aid of the apparatus shown in Fig. 1.

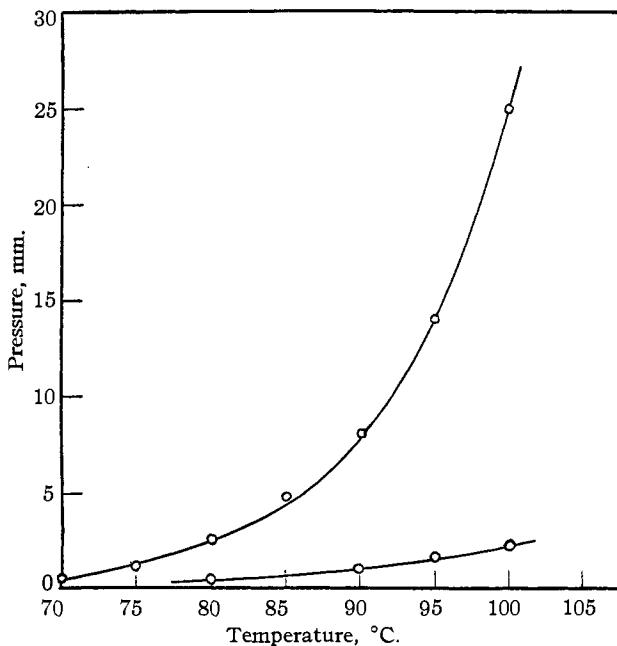


Fig. 3.—Vapor pressure of $\text{Ca}(\text{N}_3)_2 \cdot 2\text{N}_2\text{H}_4$ and $\text{Ca}(\text{N}_3)_2 \cdot \text{N}_2\text{H}_4$.

A sample of the pure dihydrinate weighing 0.1531 g. was sealed into the bulb A, which, with the manometer tube, was immersed in the glycerin bath B, so as to maintain the entire system at 100°. Successive small amounts of hydrazine vapor were pumped out, caught in the U-tubes C and D, which contained concentrated sulfuric acid, and weighed. During the dehydrization of the monosolvate it was found necessary to employ temperatures up to 120°, in view of the low vapor tension of this compound. The mercury was withdrawn from the manometer into the reservoir E during the operation of pumping.

The data plotted in Fig. 2 clearly demonstrate the existence of the compound $\text{Ca}(\text{N}_3)_2 \cdot \text{N}_2\text{H}_4$. Vapor tension measurements over a range of temperatures from 70 to 100° have also been conducted, with the result that distinct curves for the two hydrates have been obtained. The data are presented in Table I and are plotted in Figs. 3 and 4.

TABLE I

| CALCIUM TRINITRIDE DIHYDRAZINATE | | | |
|------------------------------------|----------|-------------|--------------|
| Temp., °C. | $10^4/T$ | Press., mm. | Log pressure |
| 70 | 29.15 | 0.6 | 9.778-10 |
| 75 | 28.74 | 1.2 | 0.079 |
| 80 | 28.33 | 2.5 | .398 |
| 85 | 27.93 | 4.8 | .680 |
| 90 | 27.55 | 8.0 | .903 |
| 95 | 27.17 | 14.0 | 1.146 |
| 100 | 26.81 | 25.0 | 1.398 |
| CALCIUM TRINITRIDE MONOHYDRAZINATE | | | |
| 80 | 28.33 | 0.4 | 9.602-10 |
| 90 | 27.55 | 1.0 | 0.000 |
| 95 | 27.15 | 1.6 | .204 |
| 100 | 26.81 | 2.1 | .322 |

Calcium trinitride monohydrazinate, as obtained by the foregoing procedure, is a white, fluffy powder, very soluble in water. Subjected

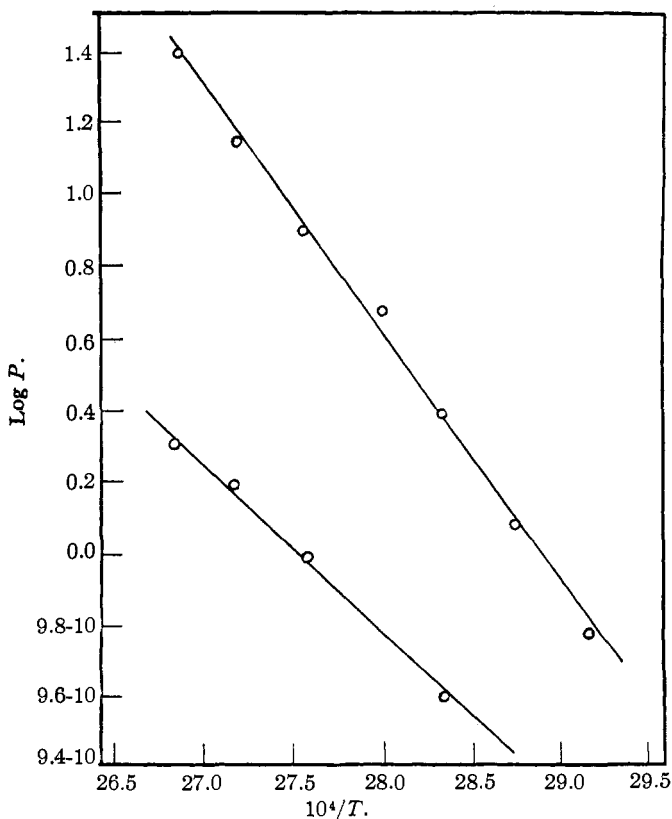


Fig. 4.

to prolonged heating it loses hydrazine very slowly at 120°, ultimately yielding the anhydrazinous salt. On the modified Maquenne block¹⁰ the monohydrizinate was found to decompose immediately, with explosive violence, at about 308°, and less rapidly at lower temperatures.

Summary

Two hydrizinates of calcium trinitride have been isolated and described. The *dihydrizinate*, $\text{Ca}(\text{N}_3)_2 \cdot 2\text{N}_2\text{H}_4$, prepared by crystallization from anhydrous hydrazine, is empirically isomeric and possibly identical with the calcium derivative of either of the two hitherto unknown hydronitrogens *pentazene-1*, $\text{HN}=\text{NNHNHNH}_2$, and *pentazene-2*, $\text{HN}(\text{NH}_2)\text{N}=\text{NNH}_2$ (*orthohydrizonitrous acid*). It may be possible, for example, that the terminal nitrogens of the pentazene-1 groups form coördinate linkages with the calcium atom, yielding a spiro structure of two six-membered rings. The *monohydrizinate* was prepared by gradual dehydrization of the disolvate.

The chemical identity of the two compounds was definitely established by means of pressure-concentration and pressure-temperature curves.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

ELECTRIC MOMENT AND MOLECULAR STRUCTURE.

VI. THE VARIATION OF ELECTRIC MOMENT WITH TEMPERATURE

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Status of the Problem

When electric moments were first investigated, the question of their possible dependence upon temperature was considered. In the cases of the simpler moments, there seemed no reason to believe that change of temperature would alter the moment of a molecule unless it caused some molecular rearrangement or a large shift of energy level. The substances which were measured over a wide range of temperature showed no departure from the linear relation between the polarization and the reciprocal of the absolute temperature required by the Debye theory that could not be attributed to the effects of molecular association or experimental error. The moments calculated from the temperature variation of the polarization of gases and liquids agreed satisfactorily with those obtained at one temperature only.¹

In these past investigations, as in the present work, the polarization, P , was calculated as

¹ Smyth, *Chem. Rev.*, 6, 549 (1929).