Dehydrogenation of 1,2,5-Triphenylpyrrolidine (V) to 1,2,5-Triphenylpyrrole (VI).—A 0.2-g. sample of the pyrrolidine which had not been separated into its diastereoisomeric components (melting range 127–170°) was heated with a mixture of 0.35 g. of chloranil and 5 ml. of *p*-cymene. The mixture darkened as the temperature was raised. When the boiling point was reached an additional 5 ml. of *p*-cymene was added and the mixture was boiled under reflux for one hour.

From the cooled reaction mixture a crystalline precipitate was removed by filtration and was shown by its alkali solubility to be the expected tetrachlorohydroquinone. No further product was precipitated from the filtrate by addition of petroleum ether. The solution was diluted with ether and extracted with an aqueous potassium hydroxide solution containing sodium hydrosulfite to reduce unchanged chloranil. The organic layer was separated, dried over potassium carbonate, and concentrated under reduced pressure to a small volume. The solid which separated was crystallized from butyl cellosolve to give white needles, m. p. 228–229°. The melting point of a mixture of this product with a sample of 1,2,5-triphenylpyrrole (m. p. 230–231°) prepared by the method of Kapf and Paal[13] was not depressed.

Ultraviolet Absorption Spectra.—The curves were plotted from data obtained with a Beckman quartz spectrophotometer, model D.U.

Summary

Reactions of 1,4-diphenyl-1-bromo-3-butene-2-one (I) with primary aromatic amines have been investigated. The initial products obtained with aniline, *p*-toluidine and *p*-chloroaniline are unsaturated arylamino ketones formed by simple replacement of the bromine atom. Treatment of these products with dilute sulfuric acid, however, converts them into 1-aryl-2,5-diphenyl-3-pyrrolidones, and provides a new synthesis of derivatives of 3-pyrrolidone.

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(13) Kapf and Paal, *Ber.*, **21**, 3053 (1888). For one of the intermediates in this synthesis, 1,2,5-triphenyl-3-carbethoxypyrrole, we observed two melting points. The value 149.5–151.5° was always obtained as the initial melting point, but samples which had resolidified in the hot melting-point bath melted at 168–170°. The previous investigators reported only the m. p. 169–170°. The following analytical results were obtained from our preparation in the low-melting form: *Anal.* Calcd. for $C_{25}H_{21}O_2N$: C, 81.72; H, 5.76. Found: C, 81.57; H, 5.68.

[Contribution from the Department of Chemistry, Polytechnic Institute of Brooklyn, and the Inorganic Chemistry Branch, Chemistry Division, U. S. Naval Ordnance Test Station]

The Oxidation of Di- and Triaminoguanidine with Potassium Iodate(1)

By Gerald I. Keim,(2) Ronald A. Henry and G. B. L. Smith

The Jamieson iodate method(3) for the quantitative determination of hydrazine and its salts has also been successfully applied to the estimation of primary hydrazino groups in such compounds as aminoguanidine,(4) benzalaminoguanidine,(4) semicarbazide and semicarbazones,(5) *p*-bromophenylhydrazine,(5) and certain hydrazides.(6) In all these cases the stoichiometric relationship can be expressed in the form

$$N_2H_5^+ + IO_3^- + H_3O^+ + Cl^- \longrightarrow N_2 + ICl + 4H_2O \quad (1)$$

where one mole of iodate is consumed per mole of hydrazino group. However, when carefully purified salts of triaminoguanidine are titrated by the Jamieson method, these results consistently show an equivalence of 2.5 moles of potassium iodate per mole of triaminoguanidine rather than the three demanded by the stoichiometric relationship (Table I). This unexpected behavior warranted a more exhaustive study as to the nature of the products formed in the reaction.

Table I

Hydrazine Nitrogen Analysis on Salts of Triaminoguanidine by the Jamieson Method

Salt	% Hydrazine nitrogen found	Theoretical % hydrazine nitrogen[a]	Theoretical % hydrazine nitrogen[b]
Nitrate	41.65 41.77	50.03	41.68
Perchlorate	34.74 34.17	41.08	34.25
Hydrochloride[c]	49.70	59.79	49.82
Picrate[c]	20.61	25.22	21.02

[a] On basis of 3 moles of potassium iodate per mole of triaminoguanidine. [b] On basis of 2.5 moles of potassium iodate per mole of triaminoguanidine. [c] Taken from the results of A. J. Foglia, B. S. Thesis, Polytechnic Institute of Brooklyn, 1943.

According to Equation (1), one mole of nitrogen should be evolved per mole of hydrazino group that is oxidized. Using a gasometric method (see experimental section) this has been found to hold almost exactly for hydrazine and hydrazine derivatives which show an equivalence of one iodate per hydrazino group in the normal Jamieson titration (Table II). As this table shows, however, triaminoguanidonium salts again behave abnormally since four moles of gas are evolved

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(1) The material in this paper pertaining to triaminoguanidine is abstracted from the thesis submitted by Gerald I. Keim to the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1944.

(2) Hercules Powder Company, Wilmington, Delaware.

(3) Jamieson, *Am. J. Sci.*, [4] **33**, 352 (1912); "Volumetric Iodate Methods," Chemical Catalog Co., New York, N. Y., 1926. It should be emphasized that the Jamieson method implies that the solutions of hydrazine derivatives are about 6 to 8 *N* with respect to hydrochloric acid prior to titration and about 3 to 5 *N* after the titration is completed. The effect of lower normalities on this titration has been discussed by Kolthoff, This Journal, **46**, 2013 (1924), and of higher normalities by Audrieth and Penneman, *Anal. Chem.*, **20**, 1060 (1948).

(4) Fuller, M.S. Thesis, Polytechnic Institute of Brooklyn, 1937; Fuller, Lieber and Smith, This Journal, **59**, 1150 (1937); Lieber and Smith, *Chem. Rev.*, **25**, 213 (1939).

(5) Smith and Wheat, *Ind. Eng. Chem., Anal. Ed.*, **11**, 200 (1939).

(6) Schaeffer and Gardner, *ibid.*, **30**, 333 (1938); Weinberger and Gardner, *ibid.*, **30**, 454 (1938).

per mole of triaminoguanidine rather than the expected three.

TABLE II

OXIDATION OF HYDRAZINE DERIVATIVES WITH EXCESS IODATE IN ACID SOLUTION—GASOMETRIC RESULTS

Salt	Moles used $\times 10^4$ A	Moles of gas (as nitrogen) evolved $\times 10^4$ B	Ratio of B to A	Expected ratio
Hydrazine sulfate	7.923	7.864	0.993	1:1
	7.708	7.738	1.004	
	7.754	7.686	0.991	
Aminoguanidonium	7.315	7.489	1.024	1:1
Nitrate	14.507	14.868	1.012	
Carbohydrazide	7.826	16.064	2.053	2:1
	7.748	16.033	2.069	
Triaminoguanidonium	3.626	14.561	4.016	3:1
Nitrate	3.015	12.208	4.049	
	2.986	11.800	3.952	
	2.716	10.638	3.917	
Triaminoguanidonium	3.123	12.264	3.927	3:1
Chloride	3.393	13.467	3.969	

Since both the nitrate and chloride give the same abnormal result, the nitrate ion cannot be considered to play a part in the formation of the extra mole of gas. This in turn indicates that the gas evolved cannot be all nitrogen. A preliminary qualitative gas analysis proved the absence of acetylenic and olefinic hydrocarbons, and of nitric oxide; it did reveal the presence of both liquifiable gas and carbon monoxide. The gas evolved during the oxidation of triaminoguanidine by potassium iodate also reduced solutions of palladium chloride, offering additional qualitative evidence of the presence of carbon monoxide. By inserting a Dry Ice–methanol trap in the gas train, the liquifiable gas was removed and the volume of gas collected was reduced by 0.5 mole per mole of triaminoguanidonium salt. This condensable gas was identified as chloroform. Furthermore, when the gas, free of chloroform, was passed through ammoniacal cuprous chloride to remove the carbon monoxide, there was another reduction in volume corresponding to 0.5 mole per mole of triaminoguanidonium salt. These results are summarized in Table III.

TABLE III

OXIDATION OF TRIAMINOGUANIDONIUM SALTS—GASOMETRIC RESULTS

Salt	Moles used $\times 10^4$ A	Moles of gas collected after passage through cold trap $\times 10^4$ B	Ratio of B to A	Moles of gas collected after passage through cold trap and through ammoniacal cuprous chloride $\times 10^4$ C	Ratio of C to A
Nitrate	3.081	10.807	3.508		
Nitrate	6.055	21.511	3.353		
Nitrate	6.067	21.294	3.509		
Nitrate	5.965	20.799	3.487	17.959	3.011
Nitrate	6.115	21.269	3.478	18.179	2.973
Nitrate	6.073	21.180	3.488	18.200	2.997
Nitrate	6.073	21.644	3.564	18.517	3.049
Chloride	6.381	22.756	3.566		
Chloride	6.694	22.861	3.415		
		Av.	3.506	Av.	3.008

Based on these observations the stoichiometric equation for the oxidation of triaminoguanidonium salts by iodate in acid solution can be written as

$$2C(NHNH_2)_3^+ + 5IO_3^- + 8Cl^- + 11H_3O^+ \longrightarrow 6N_2 + CO + CHCl_3 + 5ICl + 25H_2O$$

The true mechanism of this reaction, however, is not known yet and will be the subject of further investigations.

Although two moles of gas (within experimental error) are evolved per mole of diaminoguanidonium salt oxidized (Table IV), the titration results are both erratic and anomalous. Approximately 1.8 moles of potassium iodate, rather than the expected two, are consumed per mole of diaminoguanidine (Table V). In contrast to the behavior of triaminoguanidonium salts, chloroform and carbon monoxide are not formed as products during this oxidation since there is no reduction in the volume of gas evolved when it is passed through a Dry Ice trap and through ammoniacal cuprous chloride. Similarly, the gases evolved from the iodate oxidation of aminoguanidonium nitrate and carbohydrazide do not contain carbon monoxide or chloroform.

TABLE IV

OXIDATION OF DIAMINOGUANIDONIUM NITRATE WITH EXCESS IODATE IN ACID SOLUTION—GASOMETRIC RESULTS

Moles used $\times 10^4$ A	Moles of gas (as nitrogen) evolved $\times 10^4$ B	Ratio of B to A
4.187	8.332	1.990
6.876	13.591	1.997

TABLE V

HYDRAZINE NITROGEN ANALYSES ON CARBOHYDRAZIDE AND SALTS OF DIAMINOGUANIDINE BY THE JAMIESON METHOD

Compound	% hydrazine nitrogen found	Theoretical % hydrazine nitrogen[a]	% of theoretical value
Carbohydrazide	61.91	62.20	99.54
Carbohydrazide bisulfate	29.74	29.78	99.87
Diaminoguanidonium	33.19	36.83	90.12
nitrate	33.36	36.83	90.58
	33.58	36.83	91.18
	33.33	36.83	90.50
Diaminoguanidonium	23.39	25.81	90.62
iodide	23.38	25.81	90.59
Diaminoguanidonium sulfate	37.91	40.56	93.47
Diaminoguanidonium picrate	16.08	17.61	91.31

[a] On basis of two moles of potassium iodate per mole of carbohydrazide or diaminoguanidine.

Experimental[7]

Materials.—Triaminoguanidonium nitrate was prepared by the method of Pellizzari and Gaiter[8] from aminoguanidonium nitrate and hydrazine hydrate; m. p. 216–217°; total nitrogen, calcd., 58.70; found, 58.80.

Triaminoguanidonium perchlorate was made by a hydrazinolysis of aminoguanidonium sulfate, followed by a double decomposition with barium perchlorate; the salt melted at 133–135° after several recrystallizations from ethyl alcohol; perchloric acid, calcd., 49.20; found by nitron method, 49.75.

Triaminoguanidonium picrate, from the nitrate and picric acid in aqueous solution, had a melting point of 170–172° after several recrystallizations from water.

Carbohydrazide was made by refluxing diethyl carbonate and hydrazine hydrate in ethyl alcohol; after one recrystallization from ethyl alcohol the melting point was 155–156°; Curtius and Heidenreich[9] reported 152°. The carbohydrazide bisulfate melted at 217° (dec.) after one recrystallization from water; Curtius and Heidenreich[10] reported 218°.

Diaminoguanidonium Iodide.—S-Methylthiosemicarbazide iodide[11] (46.4 g.) was dissolved in 100 ml. of water and treated with 11.7 g. of 85% hydrazine hydrate in 25 ml. of water. This solution stood at room temperature until the evolution of methyl mercaptan had ceased, after which it was evaporated to dryness under reduced pressure. The impure product was dissolved in 200 ml. of 95% ethyl alcohol, filtered and cooled. The first crop weighed 28.6 g., m. p. 134–135°. A second crop of 6.4 g., melting at 130–133°, was obtained by evaporating the alcoholic mother liquors to 50 ml. and cooling. The total yield was 80.6%. When 10 g. of the salt was recrystallized again from 80 ml. of 95% ethyl alcohol, 5.9 g. was recovered; m. p. 134.5–135.5°.

Anal. Calcd. for CH_8N_5I: N, 32.26; I, 58.46. Found: N, 31.92; I, 58.95.

Diaminoguanidonium Picrate.—The product obtained by treating diaminoguanidonium iodide with picric acid in 95% ethyl alcohol was recrystallized from 80% ethyl alcohol; bright yellow, felted needles; m. p. 191–192° (dec.). Pellizzari and Cantoni[12] reported 191°.

Diaminoguanidonium Nitrate.—To a solution of 21.7 g. of diaminoguanidonium iodide in 50 ml. of water was added a solution of 16.9 g. of silver nitrate in 50 ml. of water. After the solution was stirred for five minutes, the silver iodide was removed by filtration and washed with 50 ml. of boiling water. The filtrate and washings were evaporated to dryness; yield, 14.1 g.; m. p. 135–140°. Two recrystallizations from 95% ethyl alcohol gave a product melting at 143–144°; reported,[8] 143°.

Diaminoguanidonium nitrate was also made by the method of Pellizzari and Gaiter[8]; m. p. 142–144° after two recrystallizations from ethyl alcohol.

Diaminoguanidonium Sulfate.—A mixture of 20.4 g. of diaminoguanidonium iodide, 14.7 g. of silver sulfate, 200 ml. of water, and 8 drops of glacial acetic acid was stirred for six hours at room temperature. The silver iodide was removed by filtration and washed with 30 ml. of hot water. The filtrate and washings were evaporated to 100 ml., refiltered, and cooled to 70°. Ethyl alcohol was added to the appearance of a permanent turbidity (about 110 ml.) and the solution cooled to 0°. A white micro-crystalline powder separated; it was removed by filtration and washed with 40 ml. of cold 50% ethyl alcohol. The yield of dried product was 8.0 g., or 64%; m. p. 230–230.5° (dec.). Recrystallization did not raise the melting point.

Anal. Calcd. for $C_2H_{16}N_{10}O_4S$: N, 50.70; S, 11.60. Found: N, 51.37; S, 11.49.

Titration.—A sample weighing between 50 and 100 mg. was dissolved in 45 ml. of cold 7.5 *N* hydrochloric acid in an iodine flask, 15 to 20 ml. of chloroform added, and the solution titrated with a 0.1 *N* solution of potassium iodate under good shaking to a disappearance of the iodine color. A final, unchanging end-point with di- or triaminoguanidonium salts was attained only very slowly.

$$\% \text{ Hydrazine nitrogen} = \frac{(\text{ml. of } KIO_3)(\text{normality})(28.016)(100)}{(1000)(\text{wt. of sample})(4)}$$

General Gasometric Procedure.—A sample weighing between 50 and 100 mg. was washed into a 250-ml. suction flask with about 20 ml. of water. The flask was fitted with a delivery tube, which was long enough to reach below the surface of the solution, and a dropping funnel through which the reagents could be added. Then 40 ml. of concentrated hydrochloric acid was added through the dropping funnel, leaving sufficient liquid in the funnel stem to serve as a liquid seal to prevent entrance or escape of gases. The side arm of the suction flask was connected to a gas buret containing a 50% solution of potassium hydroxide. The residual gases in the system were removed by a rapid stream of carbon dioxide. Then 50 ml. of a 0.1 *N* solution of potassium iodate was added through the dropping funnel, and carbon dioxide was passed through the system until the volume of gas collected in the buret remained constant for at least 10 minutes. After the isolated gases had been measured, they were analyzed in a conventional type gas analysis apparatus.

Isolation and Identification of Chloroform.—The gaseous products from the reactor were passed through a trap immersed in a Dry Ice–alcohol-bath before passing into the gas buret. Chloroform in the trap was qualitatively identified by the phenylisonitrile test and by conversion into chlorotone by reaction with acetone in the presence of powdered potassium hydroxide. An X-ray powder diagram on the material obtained was identical with that of an authentic sample of chlorotone.

Summary

Under the conditions of the Jamieson hydrazine nitrogen determination, one mole of a triaminoguanidonium salt reduces only 2.5 moles of potassium iodate rather than the expected three. Three moles of nitrogen, 0.5 mole of carbon monoxide, and 0.5 mole of chloroform are formed. The results with diaminoguanidonium salts are anomalous since one mole of nitrogen is evolved, but only about 0.9 mole of iodate is reduced, per hydrazino group.

Aminoguanidonium salts and carbohydrazide behave normally, reducing one mole of potassium iodate and yielding one mole of nitrogen per hydrazino group.

CHINA LAKE, CALIFORNIA RECEIVED APRIL 28, 1950

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(7) All melting points are uncorrected.

(8) Pellizzari and Gaiter, *Gazz. chim. ital.*, **44**, II, 72 (1914).

(9) Curtius and Heidenreich, *Ber.*, **27**, 55 (1894).

(10) Curtius and Heidenreich, *J. prakt. Chem.*, [2] **52**, 469 (1895).

(11) Freund and Paradies, *Ber.*, **34**, 3110 (1901).

(12) Pellizzari and Cantoni, *Gazz. chim. ital.*, **35**, I, 291 (1905).