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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The Preparation of Hydrazine from Urea and *t*-Butyl Hypochlorite¹

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The use of *t*-butyl hypochlorite as an oxidizing agent and as an N-chlorinating agent has been extended to urea. It has been demonstrated that *t*-butyl hypochlorite and urea react in alkaline solution to form hydrazine. The yield of hydrazine is dependent upon (a) the mole ratio of urea to *t*-butyl hypochlorite, (b) the presence of alkali, and (c) the use of an inhibitor such as gelatin. Experimental conditions are similar to those which have been found previously to govern the formation of hydrazine from *t*-butyl hypochlorite and ammonia. It has been shown spectrophotometrically that N-chlorourea is the initial product of reaction between urea and *t*-butyl hypochlorite.

Introduction

It is well-known from previous investigations²⁻⁹ that urea and alkali hypochlorites can react in alkaline solution to form hydrazine. Of the two commercial processes used for the preparation of hydrazine in this country, one employs urea as the starting material in place of ammonia. Since it was observed in a previous investigation¹ that *t*-butyl hypochlorite and ammonia react to form hydrazine, the use of this organic hypochlorite as an oxidizing agent and as an N-chlorinating agent has been extended to urea. It has been found that *t*-butyl hypochlorite reacts with urea in alkaline solution to form hydrazine. The yield of hydrazine is dependent upon three factors: (a) the mole ratio of urea to *t*-butyl hypochlorite, (b) the presence of alkali and (c) the use of an inhibitor such as gelatin.

It had been shown previously that monochloramine is the first product of reaction between *t*-butyl hypochlorite and ammonia. It has now been demonstrated, spectrophotometrically, that N-chlorourea is the initial reaction product from urea and *t*-butyl hypochlorite.

Experimental

Materials Used.—The urea employed was Merck and Co., Inc., U. S. P. material. *t*-Butyl hypochlorite was prepared¹⁰ and analyzed as described previously.¹ Standard potassium iodate was prepared by dilution of the required amount of the reagent grade chemical. Sodium thiosulfate solution was standardized against the potassium iodate solution, starch being used as the indicator. The inhibitor was Schaar pure gelatin powder.

Proof of Hydrazine Formation and Method of Analysis for Hydrazine.—The formation of hydrazine from urea and *t*-butyl hypochlorite was demonstrated by the isolation and identification of salicylalazine, m.p. 215–216°, uncor. (lit.¹¹ 214°). Hydrazine was determined quantitatively by the

indirect iodate method.¹² It was found that *t*-butyl alcohol did not interfere in this procedure.

Evidence for the Formation of N-Chlorourea from *t*-Butyl Hypochlorite and Urea.—In 50 ml. of distilled water there was dissolved 0.35 g. of urea (5.8 mmoles). Two ml. of 0.346 *M* *t*-butyl hypochlorite (0.69 mmole) in *t*-butyl alcohol was introduced and the homogeneous solution allowed to stand at room temperature (*ca.* 25°) for two days. The absorption spectrum of a portion of this reaction mixture was determined with the Cary recording spectrophotometer, a maximum being observed at 2450 Å., ϵ 244. From Fig. 1 it is readily apparent that the absorbing species cannot be urea, *t*-butyl hypochlorite or dichlorourea.¹³ It is conceivable that the peak might have been due to monochloramine, possibly formed by a hydrolysis reaction. This possibility is immediately obviated, however, since monochloramine has a molecular extinction coefficient of 416 at 2450 Å.¹⁴

Experimental Procedure.—The procedures used in the studies designed to evaluate the effect of the mole ratio of urea to *t*-butyl hypochlorite, the effect of alkali, and the use of an inhibitor were essentially the same. In studies on the yield of hydrazine as a function of the urea to *t*-butyl hypochlorite ratio, the following method was followed. Each of six erlenmeyer flasks was charged with 200 mg. of gelatin and predetermined quantities of water. The mixture was allowed to stand overnight to bring about solution of the gelatin. A 3-necked, 500-ml. flask equipped with a condenser and a stirrer was mounted on a steam-bath. Before each run, 50 ml. of 3.16 *N* sodium hydroxide solution and 3.160 g. of urea were introduced into the reaction vessel along with the aqueous gelatin solution. Then the calculated amount of 0.428 *M* *t*-butyl hypochlorite (in *t*-butyl alcohol) was added and the mixture heated under reflux and stirring for 20 minutes on the steam-bath. The resulting solution was cooled, made up to 250 ml. and a 50-ml. aliquot withdrawn and analyzed quantitatively for hydrazine by the indirect iodate method. The results are depicted graphically in Fig. 2.

To evaluate the effect of the NaOH/urea ratio (see Fig. 3), a constant mole ratio of 12.3 was chosen for the urea/*t*-BuOCl, and varying amounts of aqueous sodium hydroxide solution were employed. In the absence of base, no hydrazine could be detected. However, the presence of an oxidizing species (presumably N-chlorourea) could be demonstrated after the standard heating period of 20 minutes. Some experiments were carried out in which the mole ratio of urea to *t*-butyl hypochlorite was held constant at 1. No hydrazine could be detected when the ratio of sodium hydroxide to urea was also 1. An oxidizing species was again shown to be present. When the ratio NaOH/urea

(12) W. C. Bray and E. J. Cuy, *THIS JOURNAL*, **46**, 858 (1924).

(13) F. D. Chattaway, *Chem. News*, **98**, 285 (1908).

(14) (a) W. S. Metcalf, *J. Chem. Soc.*, 148 (1942); (b) a number of unsuccessful attempts were made to prepare N-chlorourea as described in the literature [A. Behal and A. Detoeuf, *Compt. rend.*, **153**, 681 (1911)]. The product obtained, although containing only 3% active chlorine, did, however, show an absorption maximum at 2450 Å. when measured in aqueous solution.

(1) L. F. Audrieth, Ervin Colton and Mark M. Jones, *THIS JOURNAL*, not yet published.

(2) French Patent 329,430, Feb. 16, 1903; *J. Soc. Chem. Ind.*, **22**, 1063 (1903).

(3) British Patent 392,845, May 25, 1933; *C. A.*, **27**, 5757 (1933).

(4) French Patent 743,622, April 4, 1933; *C. A.*, **27**, 3790 (1933).

(5) U. S. Patent 1,959,503, May 22, 1934; *C. A.*, **28**, 4436 (1934).

(6) German Patent 578,486, Oct. 18, 1933; *C. A.*, **28**, 1365 (1934).

(7) German Patent 735,321, April 8, 1943; *C. A.*, **38**, 2798 (1944).

(8) Swedish Patent 115,217, Oct. 23, 1945; *C. A.*, **41**, 842 (1947).

(9) German Patent 729,105, Nov. 12, 1942; *C. A.*, **38**, 381 (1944).

(10) H. M. Teeter, R. C. Bachman, E. W. Bell and J. C. Cowan, *Ind. Eng. Chem.*, **41**, 849 (1949).

(11) O. Widman, *Ber.*, **52**, 1652 (1919).

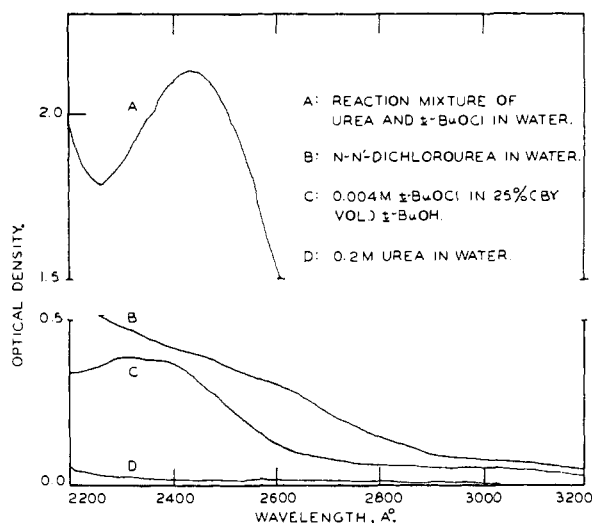


Fig. 1.—Evidence for the formation of N-chlorourea from *t*-butyl hypochlorite and urea.

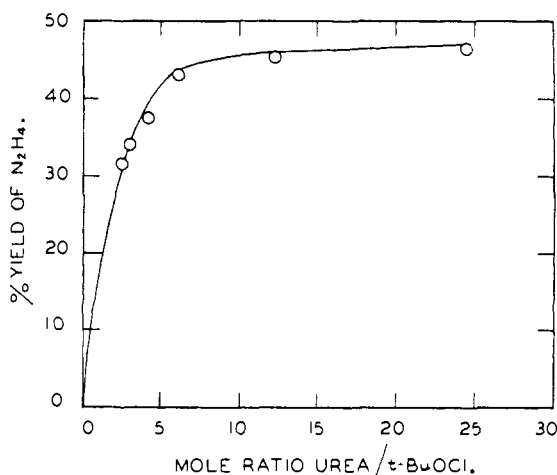


Fig. 2.—Effect of mole ratio of urea:*t*-BuOCl on yield of N₂H₄; concn. of urea constant at 52.7 mmoles; concn. of NaOH constant at 158 mmoles; gelatin constant at 200 mg.

was raised to 2 with the ratio urea/*t*-BuOCl held at 1, a 3.7% yield of hydrazine was obtained. The significance of these observations is brought out in the discussion of results.

To determine the effect of an inhibitor on the yield of hydrazine, a constant mole ratio of urea to *t*-butyl hypochlorite was selected. Also the ratio NaOH/urea was held constant at 3. Only the gelatin, weighed directly into the reaction vessel, was varied from run to run. The results are depicted graphically in Fig. 4. It is significant that substantial yields of hydrazine can be obtained even without the use of inhibitor.

An experiment was performed to demonstrate that the hydrazine formed could actually be isolated from the reaction mixture. One gram of gelatin was dissolved in 1 l. of distilled water. Ninety grams of sodium hydroxide (2.25 moles) was dissolved in 500 ml. of water and added to the aqueous gelatin solution. Sixty-eight grams of urea (1.12 moles) was introduced, and 25 g. of 98% *t*-butyl hypochlorite (0.226 mole) was added slowly to the well-stirred mixture. The contents were then heated under reflux and stirring on the steam-cone for 40 minutes. After acidifying the reaction mixture with 6 *N* sulfuric acid, 30 g. of freshly distilled salicylaldehyde was added and the mixture allowed to stand in an ice-bath for 12 hours. A yield of 19.5 g. of crude salicylalazine was realized, corresponding to a 35.9% yield of hydrazine based on the amount of hypochlorite.

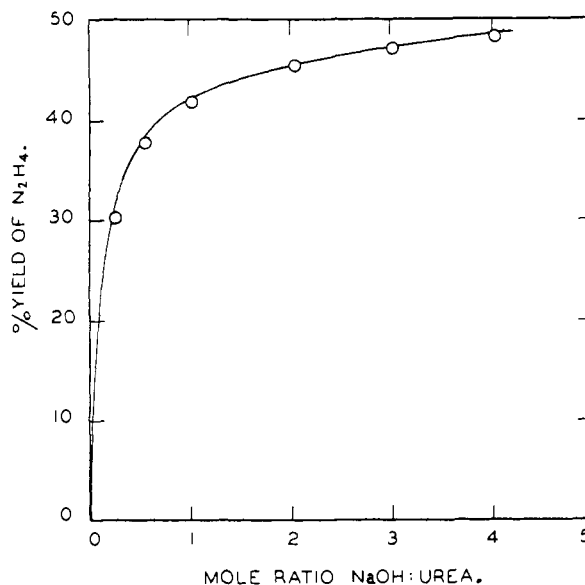


Fig. 3.—Yield of N₂H₄ as a function of NaOH mole ratio urea:*t*-BuOCl constant at 12.3; gelatin constant at 200 mg.

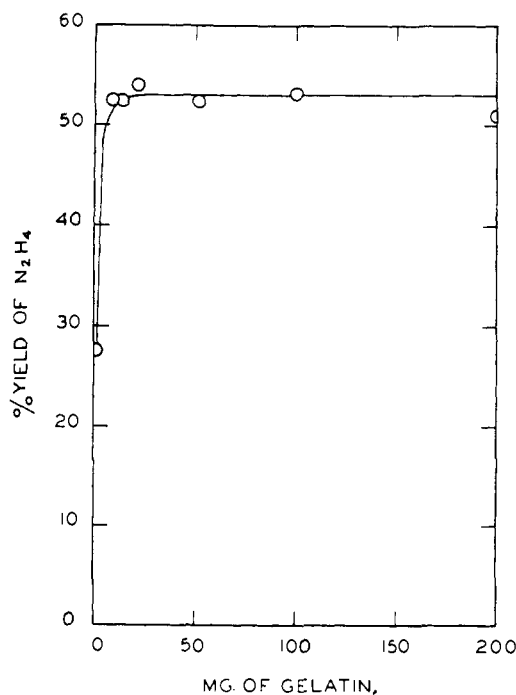
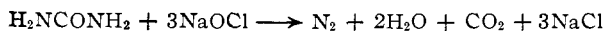


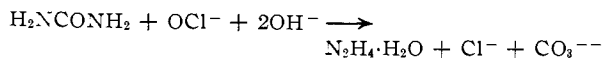
Fig. 4.—Effect of gelatin on the yield of N₂H₄; mole ratio of urea:*t*-BuOCl constant at 12.5.

Discussion of Results

The reaction between urea and alkali hypochlorite can proceed along either of two paths, depending on the presence or absence of free alkali. With no free base present, urea is oxidized quantitatively to nitrogen.

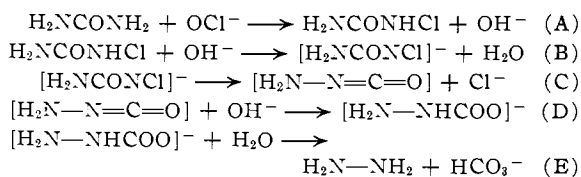


In the presence of alkali, however, urea is converted to hydrazine. It is this latter reaction which will concern us in this discussion.



Results of studies designed to illustrate how the ratio urea/*t*-BuOCl affects the yield of hydrazine at constant base concentration reveal that larger yields of hydrazine can be realized from smaller mole ratios of urea/*t*-BuOCl than were obtained in the corresponding reaction with ammonia.¹ In this investigation, for example, a 47.6% yield of hydrazine was realized using a 24.6:1 ratio of urea/*t*-BuOCl in contrast with a 43% yield of hydrazine when the ratio NH₃/*t*-BuOCl was 87.

A mechanism for the formation of hydrazine from urea and hypochlorite in basic solution was long ago proposed by Schestakoff,¹⁵ suggesting that a typical Hofmann rearrangement takes place.¹⁶



As equation A indicates, N-chlorourea is the first product of reaction between urea and hypochlorite. Although attempts to isolate N-chlorourea were unsuccessful, the spectra of solutions containing both urea and *t*-butyl hypochlorite (see Fig. 1) definitely indicate the formation of a compound containing the N-Cl linkage.¹⁷ As equations B plus D show, two moles of base are necessary before the formation of the -N₂H₃ grouping is complete. The present studies (see Experimental section) reveal that no hydrazine is detected using equimolar quantities of urea and *t*-butyl hypochlorite until a concomitant 2:1 ratio of sodium hydroxide to urea is employed. These findings are thus consistent with the proposed mechanism as outlined above. The fact that considerable yields of hy-

(15) P. Schestakoff, *J. Russ. Phys. Chem. Soc.*, **37**, 1 (1905).

(16) R. Adams, "Organic Reactions," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1946, Chapter VII.

(17) The N-Cl linkage has been shown to absorb in the vicinity of 2400-2600 Å.; monochloramine, 2450 Å. (reference 14). N-Chlorodimethylamine, 2630 Å. [I. Weil and J. C. Morris, *THIS JOURNAL*, **71**, 3123 (1949)]. N-Chlorodiethylamine, 2620 Å. [*ibid.*]; N-chlorophthalimide, 2465 Å. [H. Zimmer, this Laboratory, unpublished results]; N-chlorosuccinimide, 2459 Å. [*ibid.*].

drazine can be obtained at mole ratios NaOH/urea less than 1 (see Fig. 3) is explained by the simultaneous use of mole ratios of urea/*t*-BuOCl greater than 1.

In contrast with previous studies involving the reaction between *t*-butyl hypochlorite and ammonia it is interesting to note that considerable yields of hydrazine could be realized from urea without the use of gelatin (see Fig. 4). This observation is no doubt due to the fact that N-chlorourea, although itself not too stable, is nevertheless more stable in alkaline solution than is monochloramine, the initial reaction product of ammonia with hypochlorite. That gelatin does, however, aid in obtaining larger yields of hydrazine from urea and hypochlorite seems to indicate that N-chlorourea is also susceptible to catalytic decomposition by traces of metallic ions or that interaction between hydrazine and N-chlorourea takes place to a certain extent.

Specific reference is made to the fact that the H₂NCONCl⁻ ion is considered to be the active intermediate in this reaction and that N-chlorourea, like chloramine, will form an anionic species only in a strongly alkaline solution. It is, of course, conceivable that an intermediate N-substituted imide molecule (or radical) also forms which then immediately undergoes rearrangement to the carbonyl hydrazone. Such a rearrangement cannot occur in the Raschig synthesis where the chloramide ion by loss of chloride ion could give only the imide molecule and could therefore lead to hydrazine only through formation of H₃N → NH, a possible tautomeric form of hydrazine.

Hydrazine was also obtained from biuret and *t*-butyl hypochlorite in alkaline solution, but no advantage is gained from use of such an ammonia derivative.

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