

5. Under the present experimental conditions, the Ladenburg rearrangement does not take place to an appreciable extent. A rather unsatisfactory explanation is given for the fact that the total reaction appears to proceed to an extent greater than 100%. Rearrangement of *i*-butyl to *t*-butyl bromide appears to take place during the course of the reaction and this probably accounts for the anomalous behavior of *i*-butyl bromide.

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REDUCTION OF NITROGUANIDINE. I. PRELIMINARY STUDY OF THE OXIDATION POTENTIAL OF THE NITRO-NITROSOGUANIDINE SYSTEM¹

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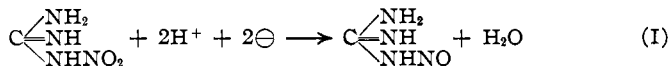
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Introduction

Nitroguanidine as an oxidizing agent has been only superficially studied and it is of peculiar interest because of the variety of reduction products which may be obtained from this substance and because of its close analogy to such important substances as nitric acid and nitrobenzene on the one hand and hydrazine and aniline on the other. Since it was thought that a knowledge of the free energy changes and the equilibrium constants for the reactions involved in the reduction of nitroguanidine would be of aid in furthering the studies on this topic, it was decided to attempt to measure the e. m. f. developed by the various nitroguanidine or derived systems.

The first system chosen for study was nitro-nitrosoguanidine, because nitrosoguanidine was the first definite reduction product of nitroguanidine known at that time and also because the preparation and properties of nitrosoguanidine were being studied in this Laboratory.

Theoretical Considerations.—It has been known from the work of Thiele in 1893² that nitroguanidine may be reduced to nitrosoguanidine in acid solution by nascent hydrogen (*i. e.*, zinc). If we assume that the reaction proceeds in accordance with the equation



¹ This paper was constructed from part of the thesis submitted by Mr. Sabetta to the faculty of the Polytechnic Institute of Brooklyn in June, 1931, in partial fulfillment of the requirements for the degree of Master of Science in Chemistry. It was presented before the Division of Physical and Inorganic Chemistry at the Eighty-second meeting of the American Chemical Society in Buffalo, N. Y., August 31 to September 4, 1931.

² Thiele, *Ann.*, **273**, 133 (1893).

the e. m. f. developed by the change from the higher state of oxidation (nitroguanidine- RNO_2) to the lower state (nitrosoguanidine- RNO) may be calculated from the familiar Peter's equation, provided the reaction is reversible

$$E_{\text{Obs.}} = E_0 - 0.03 \log \frac{(c_{\text{RNO}})}{(c_{\text{RNO}_2})(c_{\text{H}^+})^2} \quad (\text{II})$$

where $[c_{\text{H}^+}]$ has the customary meaning and (c_{RNO}) and (c_{RNO_2}) are the effective concentrations of nitrosoguanidine and nitroguanidine, respectively. If the normal oxidation potential, E_0 , is a constant when calculated by the above equation from the observed e. m. f., $E_{\text{Obs.}}$, developed by various concentrations of the reactants, the reduction of nitroguanidine to nitrosoguanidine is a reversible reaction and obeys the general law of inorganic oxidation systems.

Experimental Part

Apparatus.—The apparatus used in making these measurements of e. m. f. consisted of a Leeds and Northrup "Hydrogen Ion Potentiometer" (No. 7665), a Leeds and Northrup galvanometer with lamp and scale (No. 2420-0) and the usual accessories.

Materials: Nitroguanidine.—Pure nitroguanidine, prepared by the method described by Smith, Sabetta and Steinbach,³ was weighed and dissolved in recently boiled distilled water and diluted to the desired volume. The solutions were prepared each day because of the slow hydrolysis of nitroguanidine in water even at room temperature.

Nitrosoguanidine.—Nitrosoguanidine was prepared by reducing nitroguanidine with zinc powder in a solution of ammonium chloride.⁴ Solutions were prepared by the vigorous agitation for five minutes at room temperature of a large excess of nitrosoguanidine in contact with previously boiled distilled water. The solutions were filtered, analyzed by titration with a solution of permanganate and used immediately.

Standard Buffer Solutions.—Buffer solutions were prepared as recommended by Clark⁵ except that they were of twice the concentrations given by Clark. The solutions were checked by diluting with equal volumes of water and measuring e. m. f. with the usual hydrogen electrode.

Electrodes.—Initially, polished platinum foil, platinized platinum foil, platinum wire and silver wire were used as the inert contact electrode. Finally, either polished or platinized platinum foil (1 sq. cm. in area) was adopted. As is quite generally the case in this type of measurement, detailed attention had to be given to the cleanliness of the electrodes. What is essentially Popoff's⁶ method was used in preparing the electrodes; after thorough washing with a concentrated solution of potassium hydroxide, they were electrolyzed as anode in a concentrated solution of hydrochloric acid and then plated in the Popoff platinum solution; subsequently they were washed with distilled water, electrolyzed in a 3 *M* solution of sodium hydroxide and then in a 3 *M* solution of sulfuric acid. They were rinsed with distilled water and preserved in distilled water

³ Smith, Sabetta and Steinbach, *Ind. Eng. Chem.*, **23**, 1124 (1931).

⁴ The details of the preparation and properties of nitrosoguanidine and the analytical methods for its determination, the experimental work upon which is complete, will constitute the subject matter of the third paper of this series.

⁵ Clark, "The Determination of Hydrogen Ions," Williams and Wilkins, Baltimore, Md., 1929, pp. 200-201.

⁶ Popoff, Kunz and Snow, *J. Phys. Chem.*, **32**, 1056 (1928).

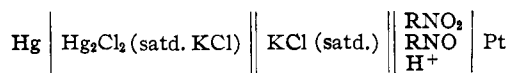
(protected from the air) until used. The polished platinum electrodes were treated in the same manner with the exception that they were not electrolyzed in the platinum solution.

Method.—In this study, mixtures of pure nitroguanidine and nitrosoguanidine were taken. Measured volumes of standard solutions of nitroguanidine and nitrosoguanidine were taken, and to this mixture was added 50 cc. of the desired buffer solution and the entire solution diluted to 100 cc. Two electrode vessels were used for the nitro-nitrosoguanidine system; in one a polished platinum electrode was in contact with the solution and in the other a platinized platinum electrode. The e. m. f. of

TABLE I
MEASUREMENTS OF THE E. M. F. OF THE NITRO-NITROSOGUANIDINE OXIDATION SYSTEM

Concentration of nitroguanidine $\times 10^{-4}$	Concentration of nitrosoguanidine $\times 10^{-4}$	pH	Observed e. m. f., volt	Calcd. normal electrode potential referred to H electrode as 0
15.44	10.00	3	0.462	0.885
30.88	10.00	3	.468	.879
46.32	14.50	3	.471	.882
15.44	12.76	3	.460	.883
20.00	20.00	3	.456	.882
				Av. .882
27.70	6.38	5	.354	.881
55.40	6.38	5	.360	.878
83.10	6.38	5	.365	.878
27.70	12.76	5	.350	.886
27.70	25.52	5	.336	.881
20.00	20.00	5	.335	.881
				Av. .881
27.70	2.52	6	.311	.886
55.40	2.52	6	.316	.882
83.10	2.52	6	.321	.881
111.00	2.52	6	.326	.883
27.70	5.04	6	.302	.885
27.70	10.09	6	.292	.885
20.00	20.00	6	.277	.883
				Av. .883
27.70	8.88	7	.209	.860
27.70	26.64	7	.207	.873
83.10	4.44	7	.223	.851
20.00	20.00	7	.202	.868
				Av. .863
27.70	4.44	8	.145	.847
27.70	8.88	8	.136	.847
83.10	4.44	8	.160	.848
20.00	20.00	8	.125	.851
				Av. .848

the nitro-nitrosoguanidine half-cell was determined by measuring the e. m. f. of the cell

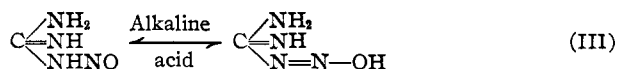


The e. m. f. of each cell (platinized electrode and polished electrode) was taken alternately every two minutes until both gave the same constant reading to plus or minus 5 millivolts (generally 1 mv.). This was usually accomplished within fifteen minutes, and equilibrium was attained by continuous tapping on the heavy copper leads to secure agitation of the solutions. The results are tabulated in Table I.

Discussion of Results

Preliminary measurements of e. m. f. developed by the nitro-nitrosoguanidine electrode in solutions where the $[c_{\text{H}^+}]$ were obtained by addition of a standard solution of hydrochloric acid gave results which followed the Peter's equation approximately and showed quite conclusively that the system under study was reversible. When $[c_{\text{H}^+}]$ was accurately controlled by means of buffered solutions, the agreement from P_{H} 3, 5 and 6 was very satisfactory, giving a maximum deviation from the mean of 4 mv. and an average of 2 mv. At P_{H} 8, however, the mean value is 34 mv. less than in the acid range, while at P_{H} 7 the individual measurements seem to oscillate between the two extreme values, but the concordance of observations is better at P_{H} 8 than in the acid range. Moreover, equilibrium is attained more quickly at P_{H} 8, and here and at P_{H} 7 a silver wire electrode gave readings checking with the carefully prepared platinum electrodes to 1 mv. These apparent discrepancies are probably not due to inaccuracies of the buffer solution at P_{H} 8.

In connection with these discrepancies, it is interesting to recall certain facts concerning the chemistry of nitrosoguanidine. This substance is readily soluble in either acidic or alkaline solution but only sparingly soluble in water. In alkaline solution it forms insoluble salts with metallic ions such as Ag^+ , Cu^{++} and Ni^{++2} , and in acid solutions salts are also formed; e. g., the hydrochloride salt is known.² These facts indicate that nitrosoguanidine is an amphoteric substance and that an intramolecular rearrangement takes place as follows



Both formulas have been suggested by Thiele.² Such changes of oxidation potential with P_{H} are quite common in organic systems,⁷ and are attributed by Clark and other workers to changes in ionization of the reductant, which cause less or more $[\text{H}^+]$ to be consumed in the

⁷ Clark, *Chem. Rev.*, **2**, 127 (1926).

reaction. This treatment leads to the conclusion that three moles of $[H^+]$ are consumed in the reduction of nitroguanidine in alkaline solution. The authors are not prepared at present to postulate a mechanism for the reaction on that assumption.

The reduction of nitroguanidine to nitrosoguanidine is a reversible reaction and proceeds in accordance with equation (I) in acid solution and according to some other mechanism in alkaline solution.

The value of the normal oxidation potential of the nitro-nitrosoguanidine system, 0.88 volt, places it between the mercuric-mercurous system, 0.92 volt, and the ferric-ferro system, 0.71 volt. This is also in agreement with other observations made in this Laboratory concerning the chemistry of nitrosoguanidine.⁸ It is worthy of note that these equilibrium potential measurements were made by using pure mixtures of the reactants.

Since the normal oxidation potential is referred to the hydrogen electrode as 0, E_0 (0.882 volt in acid solution) is a measure of the work necessary to transform one mole of nitroguanidine to nitrosoguanidine by one mole of hydrogen.⁹ Hence $(-\Delta F) = NFE = 40.7$ Kg. Cal. in acid solution. It follows logically, therefore, that the free energy of the reaction taking place in passing from acid to alkaline solution $(-\Delta F)$, is at least 1.6 Kg. Cal. This may be the free energy of ionization.

If the equation for the observed electromotive force of the nitro-nitrosoguanidine system is written in the form

$$E_{\text{obs.}} = 0.03 \log \frac{(c_{\text{RNO}_2})(c_{\text{H}})^2 K}{(c_{\text{RNO}})} \quad (\text{IV})$$

then

$$K = \frac{(c_{\text{RNO}})}{(c_{\text{RNO}_2})(c_{\text{H}})^2} \quad (\text{V})$$

at equilibrium, and when the effective hydrogen-ion concentration is one, the equilibrium constant $10^{-29.4}$ is the ratio of concentrations of nitrosoguanidine to nitroguanidine in molar acid solution existing at equilibrium with a normal hydrogen electrode. This equilibrium ratio may be computed for other hydrogen-ion concentrations, since

$$K(c_{\text{H}})^2 = \frac{(c_{\text{RNO}})}{(c_{\text{RNO}_2})} \quad (\text{VI})$$

and it is seen that this ratio drops rapidly in the alkaline range. Therefore at $P_{\text{H}} 14$ the ratio would be $10^{1.4}$. This is in accord with the observation made in this Laboratory several years ago that it was not possible to reduce nitroguanidine with zinc and concentrated sodium hydroxide.¹⁰

⁸ The effect of various reducing agents upon nitroguanidine will constitute the subject matter of the second paper of this series to be published in the near future. See also Ref. 2.

⁹ In connection with these deductions the authors are pleased to acknowledge their indebtedness to the paper by La Mer and Baker, *THIS JOURNAL*, **44**, 1954 (1922).

¹⁰ Steinbach, Thesis for M. S. in Chemistry, Polytechnic Institute of Brooklyn, 1927.

If we could maintain constancy of ratio between nitroguanidine and nitrosoguanidine, (II) could be simplified to

$$E_{\text{Obs.}} = E_0 - K'' - 0.06 \log P_{\text{H}}$$

and

$$P_{\text{H}} = \frac{K' - E_{\text{Obs.}}}{0.06}$$

and we should have a simple and convenient means of determining hydrogen-ion concentrations. An intermediate reduction product between nitroguanidine and nitrosoguanidine having the composition $2\text{RNO} \cdot 3\text{RNO}_2$ has been isolated and identified as a compound by analysis and properties.¹¹ A solution of this substance at P_{H} 7 gave the following measurements: $E_{\text{Obs.}}$, 0.206 (with polished and platinized platinum electrodes) and 0.215 (with silver wire); E_0 calcd., 0.867 volt and 0.876 volt. Moreover, it has been found possible to titrate sodium hydroxide against hydrochloric acid with this electrode.¹²

Since the normal oxidation potential, 0.88 volt, of this system is higher than that of the quinhydrone system, and higher than some values given for the hydroxyl-oxygen system, it is possible that the nitro-nitrosoguanidine electrode will not be subject to the disadvantages of the hydroquinone electrode in the alkaline region.

The authors are pleased to acknowledge their indebtedness to Professor B. P. Caldwell for his many valuable suggestions during the progress of this work.

Summary

1. The reduction of nitroguanidine to nitrosoguanidine is a reversible reaction.
2. The normal oxidation potential of the nitro-nitrosoguanidine system is 0.88 volt (free energy 40.7 Kg. Cal.) in acid solution.
3. Calculation from the equilibrium constant shows that it is not feasible to reduce nitroguanidine in strongly alkaline solution with hydrogen.
4. It is suggested that the nitro-nitrosoguanidine electrode may prove useful as a P_{H} indicator for the alkaline region.

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¹¹ This substance will be described in a subsequent communication.

¹² Further work is projected in this Laboratory to develop this electrode as a practical indicator of P_{H} measurements.