We shall next estimate the differences of energy and entropy between these two molecular forms from the temperature dependence of the 3.0μ absorption of a very dilute solution. Let the energy and the entropy of the extended form be larger by ΔE and ΔS, respectively, than those of the bent form and let κ' and κ be the molar absorption coefficient of the 3.0μ band for the pure bent form and for the mixture of the bent and extended forms, respectively. Then we have

$$\kappa = (\kappa')/\left(1 + \exp\left(\frac{\Delta S}{R} - \frac{\Delta E}{RT}\right)\right)$$

since the 3.0μ band arises only from the bent form in a very dilute solution. We cannot uniquely determine the values of ΔE and ΔS from this equation but we can show from the observed value of κ that the value of ΔS cannot be smaller than 15 e.u. If, for example, we take the reasonable values of ΔE from 3.5 to 6.0 kcal./mole, the values of ΔS are calculated as

ΔE(kcal./mole)	3.5	4.0	5.0	6.0
ΔS(e.u.)	16	15	17	19

This large value of the entropy difference would be partly explained by considering that the freedom of the internal rotation of the extended form is much greater than that of the bent form.

We know that proteins are denatured by the elevation of temperature with a large increase in entropy.[10] It is, therefore, quite interesting that the entropy increase of such a magnitude was observed for such compounds as may be considered to be structural units of a polypeptide chain.

It should be realized that the present results were all obtained in carbon tetrachloride solutions. In aqueous solutions of high dielectric constant where the *intramolecular* hydrogen bonding will be enormously suppressed, we may expect quite a different behavior with a tendency of forming more extended forms. There is no inherent inconsistency, therefore, between our results and those in the dielectric increments of aqueous solutions of some peptides.[11]

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[10] Neurath, Greenstein, Putnam and Erickson, *Chem. Revs.*, **34**, 157 (1944); M. Kunitz, *J. Gen. Physiol.*, **32**, 241 (1948).

[11] J. Wyman and T. L. McMeekin, THIS JOURNAL, **55**, 908 (1933).

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Thermal Decomposition of Guanidine Chromate and Dichromate

BY CHUK-CHING MA

Pure guanidine chromate and dichromate may be prepared from guanidine carbonate and chromic acid. When these products are heated, they decompose in an orderly manner to yield cyanamide, nitrogen, ammonia, water and Cr_2O_3. A major portion of the cyanamide formed polymerizes to dicyandiamide which in turn hydrolyzes to guanidine, ammonia and carbon dioxide. In addition to these products, ammonium carbonate and traces of melamine are also found. The residual greenish chromic oxide produces an accelerative effect on the process of hydrolysis. In the sealed tube experiments, guanidine dichromate explodes violently when heated. A less powerful effect results when guanidine chromate is heated. These indicate that the chromates of guanidine may be utilized as explosives. From the experimental results, it is concluded that the chromate ion does not oxidize the guanidine molecule as a whole, but that the guanidine rearranges into cyanamide and ammonia followed by the oxidation of ammonia by the chromate ion.

Introduction

When either ammonium chromate or dichromate is heated, or is touched with a flame or spark, a self-sustaining reaction sets in whereby the chromate ion oxidizes the ammonium ion, thereby producing chromic oxide, nitrogen and water. The same reaction does not occur in a boiling aqueous solution. The dry reaction has the unusual feature that the conditions under which it occurs are such that the chromate ion is a peculiarly effective oxidizing agent. It seemed probable that guanidine chromate or dichromate might behave similarly when heated and might yield interesting oxidation products of guanidine. However, during the course of the present investigation, it is found that the guanidine portion of the molecule rearranges to form ammonia and cyanamide, and that the ammonia thus obtained reacts with the chromate ion in the same manner as when it is already combined with it. The purpose of this study is, therefore, to formulate a series of reactions based on the available data obtained from the thermal decomposition of guanidine chromate and dichromate.

Experimental

Preparation of Guanidine Chromate and Dichromate.—The guanidine chromate and dichromate used in all the experiments were prepared from the interaction of guanidine carbonate and a calculated amount of chromic acid. The resulting salts were crystallized from aqueous solutions at 0° since they are extremely soluble in water, especially the dichromate, at room temperature. The products thus prepared were further purified by recrystallization from 50% alcohol solutions at 0°.

Anal. Calcd. for $[NH_2C(NH)NH_2]_2H_2CrO_4$: N, 35.59; Cr, 22.02. Found: N, 35.51; Cr, 21.96. Calcd. for $[NH_2C(NH)NH_2]_2H_2Cr_2O_7$: N, 25.01; Cr, 30.94. Found: N, 24.97; Cr, 30.87.

Decomposition of Guanidine Chromate (a) Qualitative Test.—Five grams of guanidine chromate was placed in an 8″ test-tube to which an air-cooled condenser was connected vertically. The test-tube was heated in an oil-bath at 160–270°. As soon as the temperature reached approximately 160°, a strong ammonia odor was noticed. Cyanamide and dicyandiamide were also identified at this stage. When the temperature rose above 190°, water vapor came off and a white crystalline sublimate condensed on the upper part of the test-tube. Under a microscope this sublimate, soluble in hot water, revealed the characteristic appearance of melamine. The aqueous solution of this substance gave a blue-green precipitate with 1% copper sulfate solution; with 0.1 *N* silver nitrate a white precipitate formed which was soluble in ammonia and in hot strong silver nitrate solution. These tests confirmed the formation of melamine, a product from the polymerization of cyanamide, as reported by Davis and Abrams.[1] In the meantime, a mass of white solid deposited inside the condenser. This was identified as ammonium carbonate. At the temperature range throughout the experiment, the color of the residue in the test-tube gradually changed from brown to black and finally to green.

(b) **Quantitative Test.**—1.761 g. (0.00746 g. mole) of guanidine chromate was placed in a 6″ test-tube and heated for 2 hours at 160–270°. The vapor passed through an air-cooled condenser and then through the absorption and the gas-collecting apparatus. In the condenser, the white solid, ammonium carbonate, deposited. The free ammonia was absorbed in standardized dilute sulfuric acid while the carbon dioxide was absorbed in a concentrated potassium hydroxide solution. Nitrogen gas (identified in a separate experiment) was collected over water in an inverted graduate cylinder and measured by the volume of water displaced. 0.1 *N* potassium hydroxide was used to titrate the excess sulfuric acid from the ammonia absorption bottle. During the first hour of decomposition, a minute quantity of white sublimate, identified as melamine, appeared near the bottom of the test-tube but gradually moved to the upper part after prolonged heating. The quantities of combined ammonia in the condenser as well as in the test-tube were determined. After 2 hours the residue was cooled, washed thoroughly with boiling water, dried and weighed. The analytical results are shown in Table I.

TABLE I

DECOMPOSITION OF GUANIDINE CHROMATE

0.02238 g. mole N_2 (1.761 g. $[NH_2C(NH)NH_2]_2H_2CrO_4$)

Product	Prod., g. mole	N_2, g. mole
NH_3 (free)	0.01564	0.00782
NH_3 (comb.)	.01845	.00923
N_2 gas	.00361	.00361
Not analyzed	.....	.00172
Residue (Cr_2O_3)[a]	.00396	.....

[a] Calculation showed that there should have been 0.00373 g. mole Cr_2O_3; 0.00396 g. mole was obtained, indicating the presence of some other stable substance in the residue.

Decomposition of Guanidine Dichromate (a) Qualitative Test.—In these experiments, tests similar to those with guanidine chromate were performed and the same set-up was employed; 5 g. of guanidine dichromate was used. Similar results were obtained except no ammonia but rather nitrogen gas was detected at the beginning decomposition stage. It was then evident that nitrogen was evolved prior to the liberation of ammonia in contrast to the observation made in the decomposition process of guanidine chromate.

(b) Quantitative Test.—1.428 g. (0.00425 g. mole) of guanidine dichromate was decomposed. After the temperature reached 190°, the experiment was temporarily interrupted, the ammonia absorption bottle disconnected from the system and the sulfuric acid in the bottle was titurated with standardized potassium hydroxide solution. It was found that no ammonia was absorbed. The absorption bottle was refilled with fresh acid and the heating was continued for 3 more hours at 190–270°. At this stage, the temperature should not be raised too fast, preferably not more than 20° per half-hour. The decomposing dichromate would be burned and a vacuum would be created if the temperature were increased rapidly to beyond this limit. The rate of decomposition of dichromate was found to be faster than that of chromate as expected on account of the higher concentration of chromate ion. The analytical results are shown in Table II.

TABLE II

DECOMPOSITION OF GUANIDINE DICHROMATE

0.01275 g. mole N_2 (1.428 g. $[NH_2C(NH)NH_2]_2H_2Cr_2O_7$)

Product	Prod., g. mole	N_2, g. mole
NH_3 (free)	0.00473	0.00237
NH_3 (comb.)	.01153	.00577
N_2 gas	.00402	.00402
Not analyzed	.....	.00059
Residue (Cr_2O_3)[a]	.00436	.....

[a] Calculation showed that there should have been 0.00425 g. mole Cr_2O_3; 0.00436 g. mole was obtained indicating the presence of some other stable substance in the residue.

Evidence of Nitrogen Formation in the Decomposition Processes.—Five grams of guanidine dichromate was decomposed by heating it in an 8″ test-tube in an oil-bath for 1 hour at 170–185°. The gas evolved was collected over water in two inverted cylinders. The possibility of the presence of nitrous oxide and nitric oxide was excluded since the gas in the first cylinder failed to support the burning of a glowing splint or a piece of ignited phosphorus. The permanent gas in the second cylinder was positively identified by its reaction at elevated temperature with magnesium and the subsequent hydrolysis of the reaction product to ammonia and magnesium hydroxide.

Confirmation of the Presence of Carbonate Ion.—One gram of guanidine chromate was heated in a test-tube at 250° until the sample was completely decomposed. The vapor evolved was directed by a glass tubing to an erlenmeyer flask containing 0.2% calcium hydroxide solution. A white precipitate, identified as $CaCO_3$, was formed.

Effect of Chromic Oxide on Hydrolysis.—In order to check the theory that chromic oxide produced an accelerative effect on the hydrolysis of dicyandiamide, two experiments were carried out. In the first one, a mixture of 2 g. of chromic oxide, 4 g. of dicyandiamide and 3 ml. of distilled water were heated in a test-tube for 15 minutes at 250°. A heavy precipitate of calcium carbonate was formed when the carbon dioxide liberated was absorbed in lime water. In the second experiment chromic oxide was omitted but with all other conditions the same. Only a faint precipitate was observed.

Sealed Tube Experiments.—A Pyrex glass tube, 40 cm. long, with a 6 mm. bore, and 1 mm. wall thickness, was filled with guanidine dichromate to about one-tenth of its volume before it was sealed. When the temperature at one end of the tube was raised to approximately 190°, guanidine dichromate exploded violently with the evolution of gases. A less violent explosion was observed when the same experiment was conducted with guanidine chromate.

Discussion of Results

The experimental results indicate that if either guanidine chromate or dichromate is heated in the dry state, it breaks down in an orderly manner to yield nitrogen, ammonia, water, cyanamide and a greenish residue of Cr_2O_3. Due to the subsequent polymerization, redecomposition and hydrolysis of the products formed at the early stage, dicyandiamide, melamine, carbon dioxide, ammonium carbonate, etc., are also observed

It appears that in the thermal decomposition of guanidine dichromate, the reaction actually proceeds in two stages. During the first stage, and at the temperature of 160–190°, the dichromate melts and then decomposes into cyanamide, nitrogen, water and a greenish residue (Reaction I). Cyanamide polymerizes to dicyandiamide (Reaction II) in the presence of water vapor produced during the course of reaction. No ammonia is detected at this stage, since any ammonia liberated by the rearrangement of the guanidine molecule is probably oxidized spontaneously to nitrogen and water by the chromate ion. In turn, the chromate ion itself continuously gains electrons as it is converted to the state of lower valency. In the second stage, and at the tempera-

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[1] T. L. Davis and A. J. J. Abrams, *Proc. Amer. Acad. Arts Sci.*, **61**, 451 (1926).

ture of 190–270°, dicyandiamide is hydrolyzed by water vapor obtained from the previous step to produce guanylurea (Reaction III), which further hydrolysis to ammonia, carbon dioxide and guanidine (Reaction IV); the latter in turn decomposes into ammonia and cyanamide. A minor quantity of the cyanamide produced polymerizes to melamine (Reaction V) while the major portion of this compound transforms to dicyandiamide which will yield more hydrolyzed products by repeating the same cycle. Due to the interaction of ammonia, carbon dioxide and water vapor, ammonium carbonate is produced (Reaction VI). It is undoubtedly true that the melamine thus obtained would be further transformed by heat to melam, melem, mellon, etc., by following the same route of transmutation as reported by Davis and Abrams.[2] Based on the experimental results, the above reactions probably take place according to the following scheme.

$$[\mathrm{NH_2{-}C(NH){-}NH_2}]_2\mathrm{H_2Cr_2O_7} \longrightarrow 2\mathrm{NH_2CN} + \mathrm{N_2} + 4\mathrm{H_2O} + \mathrm{Cr_2O_3} \qquad \mathrm{(I)}$$

$$2\mathrm{NH_2CN} \longrightarrow \mathrm{NH_2{-}C(NH){-}NHCH} \qquad \mathrm{(II)}$$

$$\mathrm{NH_2{-}C(NH){-}NHCN} + \mathrm{H_2O} \longrightarrow \mathrm{NH_2{-}C(NH){-}NH{-}CONH_2} \qquad \mathrm{(III)}$$

$$\mathrm{NH_2{-}C(BH){-}NH{-}CONH_2} + \mathrm{H_2O} \longrightarrow \underbrace{\mathrm{NH_2{-}C(NH){-}NH_2}}_{\begin{array}{c}\downarrow\\ \mathrm{NH_2CN} + \mathrm{NH_3}\end{array}} + \mathrm{CO_2} + \mathrm{NH_3} \qquad \mathrm{(IV)}$$

$$3\mathrm{NH_2CN} \longrightarrow (\mathrm{NH_2CN})_3 \qquad \mathrm{(V)}$$

$$2\mathrm{NH_3} + \mathrm{CO_2} + \mathrm{H_2O} \longrightarrow (\mathrm{NH_4})_2\mathrm{CO_3} \qquad \mathrm{(VI)}$$

In the decomposition of guanidine chromate, similar reactions have occurred except during the initial stage of decomposition and at the temperature of approximately 160°. In this stage, the chromate is first converted to dichromate and guanidine; the latter then further decomposes to cyanamide and ammonia

$$2[\mathrm{NH_2{-}C(NH){-}NH_2}]_2\mathrm{H_2CrO_4} \longrightarrow \underbrace{\mathrm{NH_2{-}C(NH){-}NH_2}}_{\begin{array}{c}\downarrow\\ \mathrm{NH_2CN} + \mathrm{NH_3}\end{array}} + [\mathrm{NH_2{-}C(NH){-}NH_2}]_2\mathrm{H_2Cr_2O_7} \qquad \mathrm{(VII)}$$

This is confirmed by the fact that ammonia is detected experimentally at the beginning stage. The dichromate thus formed then decomposes to a number of products by following the same scheme of reactions I to VI.

Based on the results from the thermal decomposition of the two guanidine salts, it is evident that the guanidine portion of the molecule rearranges to yield oxidation products of widely diversified chemical nature. In either one of the two cases, it is possible to obtain a permanent gas which was identified as nitrogen but not as oxides of nitrogen. Theoretically, the formation of these oxides is not possible since the free energy required for the materialization of any one of them is extremely high. Evidence for these postulated steps is given by the identification of the intermediate products of cyanamide and dicyandiamide. Bamberger[3a,b] reports that dicyandiamide heated with water at elevated temperature yields carbon dioxide, ammonia, etc. Davis[4] reports that the action of ammonia water on dicyandiamide when the materials are heated together in a sealed tube is a simple hydrolysis. Either reaction would account for the formation of ammonia and carbon dioxide under the conditions prevailing in the present experiments. Furthermore, since the rate of hydrolysis of the dicyandiamide increases in the presence of chromic oxide, it is concluded that the residual oxide resulting from the decomposition of guanidine chromate or dichromate has an accelerative effect on the process of hydrolysis.

The sealed tube experiments indicate that both guanidine dichromate and chromate might be used as explosives, the latter having a less powerful effect.

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[2] T. L. Davis and A. J. J. Abrams, *Proc. Amer. Arts Sci.*, **61**, 443 (1926).

[3] (a) E. Bamberger, *Ber.*, **16**, 1074 (1883); (b) **16**, 1703 (1883).

[4] T. L. Davis, THIS JOURNAL, **43**, 2230 (1921).