possibility of obtaining a gas which is largely hydrogen. If carbon monoxide is desired as well, a decrease in the steam concentration will increase the concentration of this gas.

It is to be noted that patents have been granted for the operation of these reactions at still higher temperatures.[6] A comprehensive investigation of the field has recently been published by Neumann and Jacob.[7] The reactions were carried out in both directions between 300 and 1000°. Equilibrium was reached only above 800°.

Summary

1. The reaction, $CH_4 + 2H_2O \rightleftarrows CO_2 + 4H_2$, has been studied at 500° and atmospheric pressure. Equilibrium has been approached from both sides and the value of the constant found to be 0.037 (partial pressures being expressed in atmospheres) at 505°. This is in excellent agreement with the value calculated from Lewis and Randall's free energy equations, and thus supports in particular their equation for methane in the low temperature region.

2. It is pointed out that the reactions $CH_4 + H_2O \rightleftarrows CO + 3H_2$ and $CO_2 + H_2 \rightleftarrows CO + H_2O$ are also to be taken into account at higher temperatures. Equilibrium constants at 500, 600 and 700° are given for reference.

3. Attention is called to the methane-steam reactions as a source of hydrogen and of hydrogen-carbon monoxide mixtures.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE HARRIMAN RESEARCH LABORATORY, THE ROOSEVELT HOSPITAL]

RED COMPOUNDS OF BARBITURIC ACID, PICRIC ACID AND SODIUM, OR LEAD, HYDROXIDE

BY ISIDOR GREENWALD

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Dox[1] has called attention to the red color obtained upon mixing solutions of barbituric acid, picric acid and sodium hydroxide. He stated that the color was due to the formation of picramic acid, although his only evidence therefor was the fact that the reaction mixture, treated with sulfanilic acid, sodium nitrite and acid, yielded yellow needles which appeared to be identical with those obtained from picramic acid under the same conditions.

It seemed to the writer that the matter was capable of more direct determination. His interest arose from the circumstance that Greenwald

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[6] Badische Anilin und Soda-Fabrik, British patent 12,978 (1913).

[7] Neumann and Jacob, *Z. Elektrochem.*, **30**, 557 (1924).

[1] Dox, *Z. physiol. Chem.*, **150**, 118 (1925).

and Gross[2] had found that there was no reduction of the picric acid in Jaffe's reaction for creatinine, which had also been previously ascribed to the formation of picramic acid.[3] The similarity of the color produced in the reactions of creatinine and of barbituric acid with picric acid and sodium hydroxide led to the belief that the nature of the reactions might be the same.

Just as is the case with creatinine, no color is developed when barbituric acid solutions are treated with 2,4-dinitrophenol, or with 2,6-dinitrophenol, and sodium hydroxide. With trinitro-*m*-cresol and alkali, barbituric acid gives a slowly developing orange color that is quite different from the instantaneous dark red color obtained with alkaline picrate solutions.

Solutions of barbituric acid were treated with about 1.25 equivalents of picric acid and a considerable excess of sodium hydroxide. After varying intervals, the mixtures were acidified with acetic acid and the picric acid content was determined by precipitation with nitron.[4] It was found that the loss in picric acid was very slow and, within the first fifteen minutes, quite negligible. The depth of color in the reaction mixtures, diluted to facilitate comparison, reached its maximum in about fifteen minutes, thereafter diminishing slowly.

When the proportions of barbituric acid and of picric acid were varied, it was found that increasing the concentration of either the barbituric acid or the picric acid increased the depth of color. Apparently, under the conditions originally employed, the reaction did not reach completion but proceeded to an equilibrium between the red compound and its constituents.

It was also found that the maximum color development, under the conditions employed, required more than five times the amount of alkali needed to form sodium picrate and disodium barbiturate.

When hydrochloric acid was added to a concentrated solution of barbituric acid, picric acid and sodium hydroxide, no such red compound as was obtained with similar mixtures containing creatinine,[2] instead of barbituric acid, was precipitated. The yellow precipitate seemed to consist of barbituric acid and picric acid. When, however, the alkaline reaction mixture was run into five volumes of 95% alcohol, a red, flocculent precipitate was obtained. This was filtered out, dissolved in water and reprecipitated. The material was filtered out, dried over sulfuric acid *in vacuo* and analyzed. It appeared to be a compound of 3 moles of barbituric acid, 2 of picric acid, 9 of sodium hydroxide and 1 or 2 moles of water. Whether prepared from mixtures containing one or two moles of barbituric acid for each mole of picric acid, the composition of the precipitate was the same. When, however, precipitation was made from more dilute

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[2] Greenwald and Gross, *J. Biol. Chem.*, **59**, 601 (1924).

[3] Chapman, *Analyst*, **34**, 475 (1909).

[4] Busch and Blume, *Z. angew. Chem.*, **21**, 354 (1908).

mixtures, and using more alcohol, the precipitate yielded more picric acid and contained more non-picric nitrogen and less sodium than did the preparations from the more concentrated solutions. Apparently, in the dilute solutions, more dissociation occurred and some sodium picrate and some sodium barbiturate were also precipitated.

When heated at 78°, at about 300 mm., there was no appreciable loss in weight. After drying at 100°, also at 300 mm., the loss from Preparation II was 3.1%, corresponding to about 2 moles of water. The material now yielded only 31% of picric acid, or 30% of the original weight, upon solution, acidification and precipitation with nitron. One-sixth of the picric acid had been destroyed.

That both the picric acid and the barbituric acid could be recovered from the unheated red compound was shown by suitable experiments.

When a solution of the red compound was treated with basic lead acetate solution, a brick-red precipitate was obtained. This was filtered out, washed and dried in a vacuum desiccator over sulfuric acid. Two different preparations gave slightly different results upon analysis, but in both instances the ratio of picric acid nitrogen to total nitrogen indicated that the material contained two moles of picric acid for each three moles of barbituric acid. The lead content was considerably greater than that calculated for a compound containing 9 moles of lead hydroxide. The analyses agreed best with the formula 3 barbituric acid, 2 picric acid, 11 lead hydroxide.

In another paper[5] it has been shown that the addition of alcohol to a concentrated mixture of creatinine, picric acid and sodium hydroxide yielded a red compound containing 2 moles of creatinine, 1 of picric acid, 3 of sodium hydroxide and 3 of water. It is interesting to note, in both the creatinine and the barbituric acid compounds, that the picric acid furnishes one-half of the total nitrogen and that the amount of sodium hydroxide, after allowing for that required to form sodium picrate (and monosodium barbiturate) is the equivalent of 2 moles of sodium hydroxide for each mole of picric acid. The lead barbiturate-picrate compound differs from the analogous creatinine compound in that there is no loss of nitrogen when it is treated with concentrated hydrochloric acid or 65% sulfuric acid and in that the full color value of the barbituric acid present may be obtained on treatment with more sodium picrate and sodium hydroxide

There are a number of other compounds that give similar red colors with alkaline picrate solutions. It is intended to investigate the nature of the compounds formed.

Experimental

Recovery of Picric Acid from Mixtures of Barbituric Acid, Picric Acid and Sodium Hydroxide.—To 2cc. portions of a 1% barbituric acid (anhydrous) there were added

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[5] Greenwald, *J. Biol. Chem.*, May, 1928.

5 cc. of an approximately 1% picric acid solution and 1 cc. of 10% sodium hydroxide. After varying intervals, the mixtures were acidified with acetic acid, diluted with 100 cc. of water, heated to boiling and the picric acid was precipitated with nitron. Two controls were used. One of these contained no barbituric acid; in the other, the barbituric acid was added *after* the acidification with acetic acid. The weights of the nitron picrate obtained and the amounts of picric acid they represent are shown in Table I.

TABLE I

RECOVERY OF PICRIC ACID FROM MIXTURES CONTAINING BARBITURIC ACID, PICRIC ACID AND SODIUM HYDROXIDE

	Nitron picrate, g.	Picric acid, g.
Control without barbituric acid	0.1149	0.0486
Control with barbituric acid	.1143	.0484
After standing for five minutes	.1138	.0482
After standing for ten minutes	.1129	.0478
After standing for fifteen minutes	.1121	.0475
After standing for twenty minutes	.1098	.0465
After standing for forty minutes	.1021	.0433

Rate of Color Development.—To 2cc. portions of the same 1% barbituric acid solution, there were added 5cc. portions of 1% picric acid solution. After varying intervals, 1 cc. of 10% sodium hydroxide was added. All of the mixtures were diluted to 100 cc. at the same time. That in which the reaction had proceeded for three minutes was taken as the standard and was set at 10 mm. in a Duboscq colorimeter. The readings obtained with the other solutions are shown in Table II.

TABLE II

RATE OF COLOR DEVELOPMENT

Mixture diluted after three minutes as standard at 10 mm.

Mixtures diluted after	5 min.	10 min.	15 min.	30 min.
Readings	7.65 mm.	7.00 mm.	6.70 mm.	7.30 mm.

Effect of Concentration of Sodium Hydroxide upon the Development of Color.—To 2cc. portions of the same 1% barbituric acid solution there were added 5 cc. of 1% picric acid and varying amounts of 10% sodium hydroxide. After fifteen minutes, the mixtures were diluted to 100 cc. and compared in the colorimeter, using that prepared with 1 cc. of sodium hydroxide as the standard and setting it at 10 mm. The readings obtained are shown in Table III.

TABLE III

EFFECT OF THE CONCENTRATION OF SODIUM HYDROXIDE UPON THE INTENSITY OF THE COLOR

Mixture with 1.0 cc. of 10% sodium hydroxide as standard, set at 10 mm.

Sodium hydroxide used, cc.	0.4	0.6	0.8	1.4	1.6
Readings, mm.	18.0	12.0	10.5	8.9	8.9

Effect of Varying the Proportions of Barbituric Acid and Picric Acid upon the Intensity of the Color.—Into each of a series of 100cc. volumetric flasks, there were measured 2 cc. of the same 1% barbituric acid solution and 5, 10 and 15 cc. of 1% picric acid solution. Into another flask, there were measured 4 cc. of the barbituric acid and 5 cc. of the picric acid. Water was added to make the total volume in each flask 17 cc. After adding 2 cc. of 10% sodium hydroxide, the mixtures were allowed to stand for fifteen minutes and were then diluted to 100 cc. That prepared with 2 cc. of barbituric acid and 5 cc. of picric acid was taken as the standard and was set at 10 mm. Table IV contains the readings obtained with the other mixtures.

TABLE IV

EFFECT OF VARYING THE PROPORTIONS OF BARBITURIC ACID AND PICRIC ACID UPON THE INTENSITY OF THE COLOR

Mixture containing 2 cc. of 1% barbituric acid and 5 cc. of 1% picric acid used as the standard and set at 10 mm.

Mixture	Readings, mm.
2 cc. of barbituric acid + 10 cc. of picric acid + 2 cc. of 10% sodium hydroxide	7.00
2 cc. of barbituric acid + 15 cc. of picric acid + 2 cc. of 10% sodium hydroxide	6.40
4 cc. of barbituric acid + 5 cc. of picric acid + 2 cc. of 10% sodium hydroxide	6.40

Preparation of the New Compound of Barbituric Acid, Picric Acid and Sodium Hydroxide.—(The details are those of Preparation VII.) To 8.69 g. of anhydrous barbituric acid, dissolved in 150 cc. of hot water, there was added 8 cc. of 6 *N* sodium hydroxide. To 10.36 g. of picric acid, dissolved in 300 cc. of hot water, there was added 5 cc. of 6 *N* sodium hydroxide; after mixing and cooling, 50 cc. of 6 *N* sodium hydroxide was added and the mixture was allowed to stand for ten minutes. It was then run into 3000 cc. of 95% alcohol. The flocculent precipitate was filtered out, dissolved in about 400 cc. of water and reprecipitated by running into 3000 cc. of 95% alcohol. The precipitate thus obtained was filtered out and dried at about 20 mm. over sulfuric acid; yield 21.2 g.; calculated yield about 28 g.

Analysis of the New Sodium Compound.—Weighed quantities were dissolved in water, the solution was acidified with acetic acid, and picric acid was then determined by precipitation with nitron. The filtrate from the nitron picrate was evaporated to 50 to 100 cc., about 1 cc. of nitric acid was added and the nitron nitrate was allowed to crystallize. After filtering this out, a few drops of concentrated sulfuric acid were added and the solution was evaporated in a platinum crucible. The residue was ignited and weighed. In a few instances the identity of the residue as sodium sulfate was established by conversion to barium sulfate and weighing as such. Total nitrogen was determined by the Kjeldahl method, after reduction with tin and hydrochloric acid. The same

TABLE V

ANALYSES OF THE NEW SODIUM AND LEAD COMPOUNDS CONTAINING PICRIC AND BARBITURIC ACIDS

Preparation	Total nitrogen	Picric acid	Sodium	Preparation	Total nitrogen	Picric acid	Sodium
I	13.6	37.2	17.1	Calcd. for compd. of 3 barbituric acid, 2 picric acid, 9 NaOH, 1 H_2O	13.78	37.55	16.97
II	13.5	36.5	16.6				
III	13.8	36.7	17.5				
IV (from dil. soln.)	(14.3)	(41.1)	(15.6)				
V (IV, redissolved and repptd. from concd. soln.)	13.8	38.1	17.4	Same, with 2 moles of H_2O	13.58	37.00	16.72
				Lead compound			Lead
VI	13.8	37.2	16.5	VIII (from III)	4.94	13.1	63.0
VII	13.7	37.3	17.1	IX (from VI)	4.62	12.8	65.1
				Calcd. for compd. of 3 barbituric acid, 2 picric acid, 11 lead hydroxide	4.81	13.1	65.2

values were obtained whether or not the material was first treated with dilute acetic acid.

Analysis of the New Lead Compound.—Two preparations of the lead compound were made by adding basic lead acetate solution to solutions of Preparations III and VI, respectively. The precipitates were filtered out, washed and dried in a vacuum desiccator. Picric acid was determined by dissolving weighed portions in dilute acetic acid and precipitating with nitron. Total nitrogen was determined by the Kjeldahl method, after reduction with tin and hydrochloric acid. The same values were obtained when the substance was treated directly with hot 65% sulfuric acid or with concentrated hydrochloric acid as when it was first dissolved in dilute acetic acid. Lead was determined by decomposition with sulfuric acid and also by precipitation as the sulfide from the filtrate from the nitron picrate, with subsequent oxidation to the sulfate. The amounts of lead sulfate obtained by the two methods were identical.

Isolation of Picric and Barbituric Acids from the New Substance.—Six grams of Preparation VII were dissolved in 200 cc. of water. After adding 10 cc. of concentrated hydrochloric acid, the solution was extracted with benzene in a continuous extraction apparatus, keeping the acid liquid cooled. The benzene was evaporated and the residue was dried at 110°. It weighed 2.24 g., or 37.3% of the amount of material taken. It required 91.0 cc. of 0.1073 N sodium hydroxide for neutralization. This is the exact equivalent of 2.24 g. of picric acid. The extracted liquid was evaporated, *in vacuo*, to about 60 cc. The crystals that separated were filtered out and recrystallized from water. They melted at 245°, the melting point of pure barbituric acid, and the melting point of a mixture of the two was also 245°. The nitrogen content was 17.1% and the loss in weight at 110° was 22.0%, which figures are those of the calculated nitrogen and water content of barbituric acid. The yield was 1.64 g., without correction for the solubility of barbituric acid in the 100 cc. of mother liquid. The calculated yield is 2.42 g.

The solubility of barbituric acid in water at the temperatures employed is about 1%. It is probably somewhat less in the presence of hydrochloric acid but it is not possible that the correction for solubility in the 60 cc. of acid liquid and in the 40 cc. of water employed for the recrystallization can be much less than the difference, 0.78 g., between the calculated and the observed yields.

Summary

By the addition of alcohol to a mixture of solutions of barbituric acid, picric acid and sodium hydroxide, a red precipitate is obtained. This, upon analysis, was found to contain 3 moles of barbituric acid, 2 of picric acid, 9 of sodium hydroxide and 1 or 2 moles of water. The addition of basic lead acetate to a solution of the new sodium compound yields a red precipitate which contains 3 moles of barbituric acid, 2 of picric acid and 11 of lead hydroxide.

New York City