[Contribution from the Department of Chemistry, Yale University]

NEW METHODS OF SPLITTING PYRIMIDINES. V. THE ACTION OF OXYGEN PLUS FERROUS SALTS ON THYMINE UNDER THE INFLUENCE OF LIGHT

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In previous publications[2] from this Laboratory several new methods have been described which bring about a rupture of the stable pyrimidine ring under mild conditions, as in neutral or weakly alkaline solution and at moderate temperatures. Under the conditions which have been used the products obtained from thymine are urea, acetol and pyruvic acid. A mechanism for the formation of urea and acetol from thymine has been proposed in the preceding paper of the series.[2e] The mechanism of the formation of pyruvic acid and urea has not yet been explained, although it seems most probable that the process depends upon either peroxide formation or dehydrogenation.

The observation that potassium ferrocyanide activates oxygen on exposure to sunlight[3] led to a study of the action of oxygen plus ferrous salts on thymine when illuminated by a quartz mercury arc. The final products of the reaction were found to be urea and pyruvic acid; no trace of acetol could be detected.

In this reaction, as in the other new methods of splitting pyrimidines described previously, the primary product is an intermediate compound which still contains the urea residue, a fact which is proved by the failure of the xanthydrol test for urea after an aqueous solution of thymine has been illuminated in the presence of oxygen and ferrous salts. It is necessary to hydrolyze this intermediate compound by boiling the solution with sodium bicarbonate to obtain tests for the final products, urea and pyruvic acid.

In diffused daylight (the ordinary laboratory illumination) molecular oxygen does not react with thymine in the absence of ferrous salts.[2] In the presence of ferrous salts, however, a small quantity of urea is formed. When an aqueous solution of thymine in an atmosphere of oxygen is exposed to a quartz mercury light for 12 hours, the pyrimidine is split into urea (3.8%) and pyruvic acid. The presence of ferrous sulfate or potassium ferrocyanide in the reaction mixture greatly increases the extent of the split, the former having the greater effect.

It has been shown also that when the experiments are carried out in an

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[2] Johnson and Baudisch, (a) This Journal, **43**, 2670 (1921). (b) *Ber.*, **55**, 18 (1922). Pfaltz and Baudisch, (c) This Journal, **45**, 2972 (1923). (d) Bass and Baudisch, *ibid.*, **46**, 181 (1924). (e) Baudisch and Bass, *ibid.*, **46**, 184 (1924).

[3] Baudisch, *Ber.*, **54**, 413 (1921). Baudisch and Bass, *ibid.*, **55**, 2698 (1922).

atmosphere of nitrogen instead of oxygen, no split occurs. Traces of urea which were found in some reaction mixtures are probably due to the presence of small quantities of oxygen in the nitrogen.

The results of the investigation are summarized in Table I.

TABLE I

COMPARISON OF THE FORMATION OF UREA AND PYRUVIC ACID FROM THYMINE UNDER DIFFERENT CONDITIONS

In each experiment 0.4000 g. of thymine was dissolved in 300 cc. of water. The duration of each reaction was 12 hours. In Nos. 2, 7, 8, 9, 10, and 16 the catalyst was 0.1 g. of $FeSO_4.7H_2O$; in Nos. 11, 12 it was 0.1 g.; in Nos. 13, 14, 17 it was 0.15 g. of $K_4Fe(CN)_6$. Six g. of $NaHCO_3$ was used in Nos. 1, 2, 3, 4, 7, 8, 11–17. The product was distilled in Nos. 1, 2, 3, 4, 8, 9, 11–17.

No.	Urea	Acetol test	Pyruvic acid test	No.	Urea	Acetol test	Pyruvic acid test
Experiments with oxygen (diffused daylight)							
1	0[20]	....	...	10	0	....	...
2	Traces[20]	....	...	11	10.2%	....	...
Experiments with oxygen plus light							
3	3.8%	....	...	12	....	Negative	Positive
4	....	Negative	Positive	13	10.8%	....	...
5	0	....	...	14	....	Negative	Positive
				Experiments with nitrogen plus light			
6	0	....	...	15	0[a]	....	...
7	42.4%	....	...	16	0[a]	....	...
8	....	Negative	Positive	17	0[a]	....	...
9	Traces	....	...	..	....	....	...

[a] Traces of urea were observed in some experiments. These traces were probably formed as a result of the presence of small quantities of oxygen in the nitrogen.

The study of this reaction is to be extended to other pyrimidines and to purines.

Experimental Part

Apparatus.—A 220 volt d. c. Uviarc Laboratory Outfit, vertical type, was used in all experiments. The reactions were carried out in a 600cc. round-bottom flask of transparent quartz which was immersed in a thermostat at room temperature. The water level in the thermostat was kept a few millimeters below the level of the solution in the reaction flask. The lamp was adjusted so that the quartz tube was 15 cm. from the level of the solution in the reaction flask.

Analytical Methods.—Urea was determined quantitatively by the method of Fosse.[4] Tests for acetol and pyruvic acid were made according to the methods of Baudisch[5] and Baeyer,[6] respectively. The application of these three tests to the degradation products of thymine has been discussed in detail by Pfaltz and Baudisch.[20]

Procedure.—The weighed quantity of thymine, dissolved in boiled distilled water, was introduced into the quartz reaction flask. In experiments with ferrous salt catalysts the salt was also dissolved in boiled water. The reaction flask was then adjusted in the thermostat.

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[4] Fosse, *Ann. chim.*, [9] **6**, 13 (1916).

[5] Baudisch, *Biochem. Z.*, **89**, 279 (1918).

[6] Baeyer, *Ber.*, **15**, 2856 (1882).

A rubber stopper, covered with tin foil and equipped with a gas inlet tube (extending to the bottom of the flask) and a gas outlet tube, was then introduced into the neck of the flask. Oxygen was passed through the solution for three hours before exposing to the mercury arc.[7]

After the exposure was completed the reaction mixture was transferred to an ordinary flask and the required quantity of solid sodium bicarbonate was added. The solution was then distilled to small volume. Acetol tests were made on the distillate and pyruvic acid, and urea tests on the residue.

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Summary

1. When aqueous solutions of thymine in an atmosphere of oxygen are illuminated by a quartz mercury arc, the pyrimidine is split to some extent into urea and pyruvic acid; no acetol is formed.

2. The reaction is catalyzed by ferrous sulfate and by potassium ferrocyanide, the former being the more active catalyst. The products obtained are the same as those in the absence of catalysts.

3. No split occurs in an atmosphere of nitrogen, even in the presence of ferrous sulfate or potassium ferrocyanide.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

ADDITION REACTIONS OF THE PHOSPHORUS HALIDES. VIII. KINETIC EVIDENCE IN REGARD TO THE MECHANISM OF THE REACTION

BY J. B. CONANT AND V. H. WALLINGFORD

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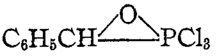
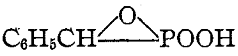
In one of the earlier papers of this series[1] the mechanism of the reaction between phosphorus trichloride and benzaldehyde was investigated. It was shown that the halide and aldehyde combined in the absence of any other substance to form an addition product to which we ascribed the formula  $C_6H_5CH{<}\overset{O}{\rule{2em}{0.4pt}}{>}PCl_3$ (I), because on decomposition with water (or acetic acid) a "phostonic" acid,  $C_6H_5CH{<}\overset{O}{\rule{2em}{0.4pt}}{>}POOH$ (II), was formed. This monobasic acid was transformed into the hydroxy dibasic acid, C_6H_5-$CHOHPO_3H_2$, on boiling with water. Since the phostonic acid was found in the product of the reaction of benzaldehyde, phosphorus trichloride and acetic acid (or acetic anhydride), it was concluded that the compound I was intermediate in the reaction which took place in these solvents. Ac-

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[7] In experiments with nitrogen, the gas was freed from traces of oxygen by passing it through a strong alkaline solution of pyrogallol and through an aqueous suspension of ferrous hydroxide.

[1] THIS JOURNAL, 42, 2337 (1920).