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Contract No. W-7405-eng-48

THE PERMANGANATE OXIDATION OF URACIL AND 5-NITROURACIL

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November 11, 1952

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ABSTRACT

Permanganate oxidation of uracil-4-C^{14} and 5-nitrouracil-4-C^{14} indicates that in the two compounds ring cleavage occurs both between carbons 4 and 5 and carbons 5 and 6.

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(**) The work described in this paper was sponsored by the U. S. Atomic Energy Commission.

The reaction of uracil with potassium permanganate to yield carbon dioxide and oxaluric acid has been of use in the degradation of the pyrimidine ring.[1, 2]

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1. M. R. Heinrich and D. W. Wilson, J. Biol. Chem. 186, 447 (1950).
2. M. Edmonds, A. M. Delluva and D. W. Wilson, J. Biol. Chem. 197, 251 (1952).

The similar oxidation of 5-nitrouracil has been used by Lagerkvist to obtain the distribution of carbon-14 in the uracil of the nucleic acids of rats following the injection of radioactive bicarbonate.[3] In this work the assumption was made, following Offe,[4] that the oxalic acid fragment obtained upon hydrolysis of oxaluric acid was derived from carbon atoms 4 and 5 of the pyrimidine.***

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3. U. Lagerkvist, Acta Chem. Scand. 4, 1151 (1950).
4. G. Offe, Ann. 353, 267 (1907).

(***) The numbering of the pyrimidine ring is in conformance with current usage of Chemical Abstracts.

It was felt that the determination of the course of these reactions might prove of value in tracer experiments on the biological synthesis of the pyrimidine compounds. Accordingly, uracil-4-C^{14} and 5-nitrouracil-4-C^{14} were synthesized and subjected to permanganate oxidation. As shown in Table I, high percentages of the isotope were found in each carbon dioxide and the oxalic acid fraction of the two pyrimidines, indicating that ring cleavage had occurred both between carbons 4 and 5 and carbons 5 and 6, with the last reaction predominating to some extent. In its present form the method offers little value as a degradative procedure, and therefore the interpretation of the results of Lagerkvist is seriously in doubt.

Table I

Permanganate Oxidation of Uracil-4-C^{14} and 5-Nitrouracil-4-C^{14}

Compound	Amt. Used mg.	Amt. Recovered (as $BaCO_3$)	Specific Activity c./min./mg. $BaCO_3$	Total Activity c./min.
Uracil-4-C^{14}	75			24.7×10^5
CO_2		115	7900	9.1×10^5
Oxalate		160	6600	10.6×10^5
5-Nitrouracil-4-C^{14}	47.5			21.6×10^4
CO_2		53	1350	7.1×10^4
Oxalate		72	1140	8.2×10^4

Experimental

Uracil-4-C^{14}. The method of Davidson and Baudisch[5] was used for the synthesis of uracil from urea and a sample of malic acid-4-C^{14} prepared in this laboratory by methods recently described.[6] The identity and purity of the twice-recrystallized

5. D. Davidson and O. Baudisch, J. Am. Chem. Soc. 48, 2379 (1926).

6. E. C. Jorgensen, J. A. Bassham, M. Calvin and B. M. Tolbert, J. Am. Chem. Soc., 74, 2418 (1952).

uracil-4-C^{14} were established by the determination of the ultraviolet absorption spectrum in 0.01 N HCl. Both the ϵ_{max} and the ratio of optical densities at 260 to 280 mμ agreed to within 1% with published data.[7]

7. J. M. Ploeser and H. S. Loring, J. Biol. Chem. 178, 431 (1949).

5-Nitrouracil-4-C^{14}. The method of Johnson and Matsuo[8] was used for the preparation of 5-nitrouracil from a portion of the uracil-4-C^{14} diluted somewhat with

8. T. B. Johnson and I. Matsue, J. Am. Chem. Soc. 41, 782 (1919).

non-radioactive uracil. The gain in weight during this process was 94% of theory. The material was recrystallized once from water.

Oxidation of Uracil-4-C^{14}. The procedures described by Heinrich and Wilson[1] for the cleavage of the pyrimidine ring, collection of the CO_2, hydrolysis of the oxaluric acid, precipitation of calcium oxalate and its subsequent oxidation to CO_2 were followed closely, except that the pH of the reacting solution was maintained between 5 and 7 with the aid of a pH meter.

Oxidation of 5-Nitrouracil. The method of Offe[4] was followed for the oxidation step, followed by procedures similar to those mentioned for uracil.

References

1. M. R. Heinrich and D. W. Wilson, J. Biol. Chem. 187, 447 (1950).
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3. U. Lagerkvist, Acta Chem. Scand. 4, 1151 (1950).
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For publication in the Journal of Americal Chemical Society.