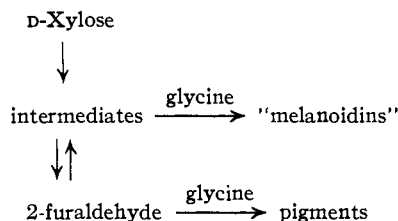


as when 2-furaldehyde is reacted with a large excess of glycine. 2-Furaldehyde is undoubtedly a member of a complex system of the type shown



It is probable that the small amount of 2-furaldehyde present in the D-xylose-glycine system represents a by-product which may form pigmented products of its own type. It may also react by ring-opening to form intermediates in common with D-xylose and from these would be obtained "melanoidins" of similar structure. Such a view would be in accordance with the work of Akabori.^{4e} For a hexose, as D-glucose, 5-(hydroxymethyl)-2-furaldehyde would play a role entirely analogous to 2-furaldehyde.¹⁴

Experimental

Materials.—The colorless 2-furaldehyde required in this comparative study was obtained from a commercial sample (Baker Chemical Co.) that had been freshly twice-redistilled under diminished pressure. The D-xylose used was of C. P. grade (Pfanstiehl Chemical Co.).

Preparation of Colored Products.—Three general procedures were used.

Procedure 1.—A mixture of 3.7 g. (0.025 mole) of D-xylose (or 2.4 g. of 2-furaldehyde), 18.7 g. (0.250 mole) of glycine and 200 ml. of water was heated at 95° for a designated time. The contents were transferred into a cellophane bag (made of Osmosis Membrane 70160-B, a product of the Central Scientific Co., Chicago, Ill.) and dialyzed against distilled water until the solution in the bag gave negative ninhydrin and Molisch tests (three days). The dialyzed solution was concentrated (in the case of 2-

furaldehyde, the solution was centrifuged before concentration to remove the water-insoluble colored product; insoluble products 8 and 9 of Table I were so separated from the soluble products 6 and 7, respectively) under reduced pressure to about one-third of the original volume and coagulated by adding five times the volume of dioxane (ethanol was used in several experiments; cf. Table I). The precipitate formed was collected by centrifuging, washed successively with ethanol, acetone and ether, and finally dried in the air (products 1 and 5-7 in Table I).

Procedure 2.—Thirty grams (0.20 mole) of D-xylose (or 19.8 g. of 2-furaldehyde), 15.0 g. (0.20 mole) of glycine and 200 ml. of water were mixed and heated at 95° for two days (cf. Table I). The reaction mixture was filtered under suction and the water-insoluble colored product washed with water, ethanol, acetone and ether (products 4 and 10 in Table I). The filtrate, in the case of D-xylose, was highly colored and was dialyzed and coagulated with ethanol as in procedure 1 (product 2 in Table I).

Procedure 3.—A solution containing 7.5 g. (0.05 mole) of D-xylose (or 4.8 g. of 2-furaldehyde), 3.8 g. (0.05 mole) of glycine and 200 ml. of water was heated under reflux for forty hours. The colored material formed was insoluble in water and was separated from the starting materials by filtration as in procedure 2 (products 3 and 11 in Table I).

Summary

1. A comparative study under definitive conditions has been made of the coloration of D-xylose-glycine and 2-furaldehyde-glycine solutions. The results indicate that 2-furaldehyde can be a color precursor in the "browning" of D-xylose solutions.

2. Brown materials have been prepared, under a variety of conditions, from glycine and D-xylose and compared with those formed from glycine and 2-furaldehyde. Their elementary composition, absorption spectra (ultraviolet, visible and infrared) and behavior toward bromine have been studied and compared.

3. The results show that the products obtained from 2-furaldehyde approach in properties those from D-xylose as their conditions of formation approach those of the latter.

COLUMBUS, OHIO

RECEIVED APRIL 3, 1950

(14) M. L. Wolfrom, R. D. Schuetz and L. F. Cavaliere, *THIS JOURNAL*, **70**, 514 (1948).

[CONTRIBUTION FROM THE INSTITUTE FOR ENZYME RESEARCH, UNIVERSITY OF WISCONSIN, AND THE TEXAS RESEARCH FOUNDATION]

Chemical Oxidation of Organic Acids. I. Some Observations on the Oxidation of Propionate by Alkaline Permanganate^{1,2}

BY HENRY R. MAHLER AND AMMARETTE ROBERTS

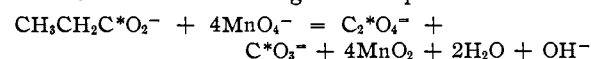
In 1941 and 1942, Nahinsky, Ruben and co-workers published two papers³ dealing with the oxidation of propionate by alkaline permanganate. They elucidated the mechanism of this reaction by means of C¹¹, a radioactive isotope of carbon of short half-life, and the only radiocarbon tracer

(1) The experimental work reported in this communication was carried out at the Texas Research Foundation, Renner, Texas.

(2) Presented before the Division of Physical and Inorganic Chemistry at the 117th meeting of the American Chemical Society at Detroit, Michigan, April 17, 1950.

(3) P. Nahinsky and C. N. Ruben, *THIS JOURNAL*, **63**, 2275 (1941); P. Nahinsky, C. N. Rice, S. Ruben and M. D. Kamen, *ibid.*, **64**, 2299 (1942).

then available for chemical experimentation. Employing propionate-1-C¹¹, their most remarkable results were those obtained in a strongly alkaline medium. Under those conditions, the oxalate formed according to the equation



incorporated the bulk of the radioactivity, *i. e.*, 87%.

We have undertaken to re-investigate these experiments utilizing propionate-1-C¹⁴. Two related aims prompted us to this endeavor: the

use of the long-lived isotope makes possible increased ease and convenience in the various chemical operations, and might give rise to greater refinement in the counting and assay steps, leading to increased accuracy. Secondly, considerable interest has been aroused of late by the isotope effect.⁴ That the substitution of a different isotope at a particular atomic location in a molecule should give rise to a difference (when comparing the isotopic isomers) in the rates of a reaction involving rupture of a bond at this locus follows from first principles and cannot be in doubt. The magnitude of this effect, however, is difficult to predict, and considerable controversy attends its possible extent and significance.⁵ In the case of carbon, the most striking results observed so far have been in reactions involving scission of carbon-carbon bonds.⁴ Our investigation, ideally, should provide us with a possible means of estimating the isotope effect, in this particular case, by comparing the distribution of radioactivity obtained with C¹⁴ to the distribution obtained by the earlier investigators by means of C¹¹.

In the mechanism postulated by Nahinsky and his co-workers, based on their experiments with propionate and its hydroxylated substitution products, pyruvate is named as an intermediate. In view of the known proclivity of α -ketoacids toward decarboxylation, especially in an oxidizing environment, it appeared of interest to determine the importance of this reaction under our experimental conditions. In this manner, with the aid of pyruvate-2-C¹⁴, it should be possible to decide whether this decarboxylation, if present at all, has to be taken into consideration when reformulating the mechanism of propionate oxidation.

Experimental⁶

Materials and Methods.—The propionate-1-C¹⁴ and the pyruvate-2-C¹⁴ were synthesized by us utilizing modifications of published procedures.

Oxidations were carried out in 30 ml. pear-shaped flasks, equipped with reflux condensers, at 100°. The reactions were allowed to proceed for 30 minutes for propionate, and 20 minutes for pyruvate. These reaction times could be shown to be sufficient for complete disappearance of all reactants, as determined by standard methods. At the end of this period the flasks were quickly chilled by immersion in cracked ice. Excess permanganate was destroyed with hydrogen peroxide and the manganese dioxide removed by centrifugation. The precipitate was then washed several times with boiling water.³ The supernatant and washings were diluted to 200.00 ml. This solution was then split into two equal fractions.

Fraction 1 was acidified with acetic acid, calcium acetate was added, the calcium oxalate precipitated, the mixture

(4) E. g., P. E. Yankwich and M. Calvin, *J. Chem. Phys.*, **17**, 109 (1950); J. Bigeleisen, *ibid.*, **17**, 425 (1949); J. Bigeleisen and L. Friedman, *ibid.*, **17**, 998 (1949).

(5) Cf. ref. 4 and P. McElchran, J. Lindsay and T. Thode, *J. Chem. Phys.*, **17**, 589 (1949); J. Bigeleisen, *ibid.*, **17**, 675 (1949); **17**, 344 (1949); *Science*, **110**, 74 (1949); K. Pitzer, *J. Chem. Phys.*, **17**, 1341 (1949).

(6) The C¹⁴ was obtained by the Texas Research Foundation on allocation from the Isotopes Division, U. S. Atomic Energy Commission.

digested in the usual manner, and the product isolated. After drying, a portion of known weight was used for radioactivity measurements. The remainder was dissolved in hot sulfuric acid and the oxalate determined volumetrically by means of permanganate. This procedure was necessary since occasionally the gravimetric method alone gave high results.

Fraction 2 was placed in a carbon dioxide generator and the carbon dioxide, formed by acidification of the solution with sulfuric acid, was swept by means of nitrogen into two bubble traps, filled with 0.1 *N* sodium hydroxide. Absorption was complete and quantitative after 60 minutes sweeping, as determined by experiments employing known quantities of carbonate. Under these conditions no carbonate could ever be detected in the second trap. The carbonate was then precipitated as barium carbonate by the addition of ammonium chloride and barium chloride in the customary manner.⁷ The barium carbonate was dried, weighed and its radioactivity determined. A blank was always run with all reagents added, omitting only the propionate, and carried through all the steps. Its results were then subtracted from the barium carbonate values.

In the pyruvate experiments the procedure was modified as follows: fraction 2, after all the carbon dioxide had been swept out, was placed in a steam distillation apparatus, and the acetic acid steam-distilled. The acetic acid was determined in the steam distillate by titration with standard base. The above procedure, when run with known quantities of carbonate and acetate, gave quantitative recoveries. For activity measurements all solvents were removed *in vacuo* and the sodium acetate counted as such, by plating an aliquot of a solution prepared by dissolving the dried, weighed sodium acetate in a known volume of water.

Radioactivity Determinations.—All assays were made with a "Tracerlab TGC" tube with a mica window thickness of 1.96 mg./sq. cm. and using a "Nuclear Model 163" scaler. Precipitates and solutions were deposited on one-inch aluminum planchets from a special brass deposition cup for solids,⁸ and employing 0.100 ml. micropipets for solutions. In that case the planchets were placed on a rotating turntable and the solvent allowed to evaporate in a stream of dry air.

All counts were corrected for self-absorption, coincidence and back-scattering and were determined for triplicate samples.

All counts were taken for a sufficient length of time so as to obtain an intrinsic standard counting error of \leq one per cent.

Results and Discussion

Oxidation of Propionate-1-C¹⁴.—The pertinent data are summarized in Table I. It can be seen that under properly controlled conditions

TABLE I
OXIDATION OF PROPIONATE-1-C¹⁴ WITH ALKALINE PERMANGANATE

Compound	Mmoles found or added	Counts/min.	Specific activity (counts/min./mmole)
Propionate	0.524	32100	61300
Carbonate	.530	3325	6350
Oxalate	.520	29400	57000

All analytical and counting data \approx 2%. Conditions of the experiment: 1 ml. of 0.524 *M* solution of propionate incorporating 32,100 cts./min. 5 g. NaOH (10 ml. of 50 per cent. solution); 0.400 g. KMnO₄ (2.52 mmol.); 30 min. at 100°. Found: oxalate/carbonate = 0.98 \approx 2%.

(7) M. Calvin, C. Heidelberger, J. C. Reid and B. M. Tolbert, "Isotopic Carbon," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 85.

(8) Cf. ref. 7, p. 118.

Summary

1. Comparison of results obtained for the alkaline permanganate oxidation of propionate- $1-C^{14}$ with those for the corresponding C^{11} compound show certain differences: 90% of the activity is incorporated in the oxalate fraction in the former case compared to 87% for the latter. Since these differences may be within the limits of experimental error, their significance is hard to assess. Thus the presence of a measurable isotope effect in this case could not be definitely determined.

2. Since pyruvate has been postulated as an

intermediate in propionate oxidation, the behavior of pyruvate- $2-C^{14}$ in alkaline permanganate was investigated. Under these conditions approximately 80% of the pyruvate is transformed into oxalate and carbonate, with the former retaining all the activity; 20% of the pyruvate is decarboxylated, however, yielding labeled acetate and inactive carbonate. Thus, decarboxylation is a minor pathway in pyruvate oxidation under these conditions and has to be taken into consideration when discussing the mechanism of propionate oxidation as well.

MADISON 6, WISCONSIN

RECEIVED MAY 8, 1950

[CONTRIBUTION FROM THE DEPARTMENT OF ORGANIC CHEMISTRY OF THE HEBREW UNIVERSITY, AND THE LABORATORIES OF THE SCIENTIFIC DEPARTMENT, MINISTRY OF DEFENCE]

The Oxidation of Carbon Black by Solid Potassium Perchlorate

BY SAUL PATAI AND E. HOFFMANN

Introduction

Combustible mixtures of solids have been described as giving a self-sustaining reaction only at temperatures higher than the decomposition point of the oxidant¹ or after initiation by local ignition.² In several cases, a surprisingly low

temperature of initiation has been observed,³ and although no information is available as to the mechanism and kinetics of the initiation reaction, Schneider⁴ has assumed that reaction of mixtures of organic substances and inorganic oxidants is dependent on the primary liberation of free oxygen by decomposition of the oxidant.

We studied the behavior of the mixture of potassium perchlorate and carbon black. In the temperature range of 320–385°, it reacted according to the equation $KClO_4 + 2C = 2CO_2 + KCl$. In most cases, 60–90% of the mixture reacted in this manner smoothly in the course of five hours.

Experimental

The apparatus consisted of an electric furnace and a cylindrical glass reaction chamber with a well for the thermocouple; this was connected to a sensitive millivoltmeter permitting readings within 0.5°. An elongated part of the reaction chamber protruded from the furnace; a glass spoon joined to a small steel block could be introduced into the reaction chamber or withdrawn from it into the cold part of the apparatus by means of an electromagnet. The apparatus was connected to a mercury manometer, a rotary vacuum pump and an Orsat-type gas analyser.

Preparation of Samples.—Pure potassium perchlorate, ground to 200 mesh, and a commercial carbon black (average diameter of particles, 0.005 mm.) were used. The latter, after drying at 120°, contained about 0.5% of volatile matter (at 300° *in vacuo*) and 1.5% of ash, consisting of alkali sulfates and carbonates and traces of iron.

The components were thoroughly mixed in the desired proportions (for each mol. of carbon black: 0.25; 0.50; 0.75; 1.0 and 5.0 mol. of perchlorate), wetted with about 5% water and pressed into tablets under a pressure of 800 atm. The tablets were dried for four hours at 120° and degassed at 250° *in vacuo*. This procedure gave reproducible results and no change in reaction rate was observed

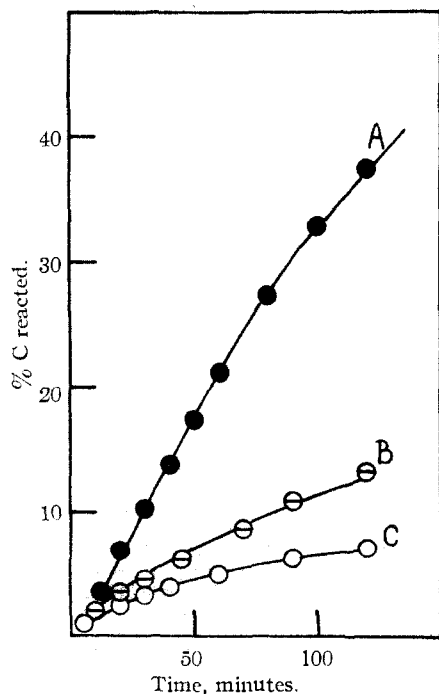


Fig. 1.—Reaction rates of carbon-potassium perchlorate (1:0.5 mole) mixtures at 367°: A, standard sample, mixed, wetted and pressed at 600 atm.; B, same mixture, ground together but not pressed; C, mixed by shaking only.

(1) Davis and Hardesty, *Ind. Eng. Chem.*, **37**, 59 (1945).

(2) Taylor, *Ind. Chemist*, **24**, 289 (1948); U. S. Patent 2,159,234 [C. A., **33**, 7116 (1939)].

(3) Taradoire, *Documentation Sci.*, **6**, 232 (1937) [C. A., **32**, 1455 (1938)]; Heertjes and Houtmann, *Chem. Weekblad.*, **38**, 85 (1941) [C. A., **36**, 5349 (1942)]; Heinrich, *Forstarchiv*, **16**, 189 (1940) [C. A., **36**, 2146 (1942)]; Elliott, U. S. Bur. Mines Repts. Invest. No. 4244 (1948) [C. A., **42**, 3179 (1948)].

(4) Schneider, *Z. ges. Schiess u. Sprengstoffw., Nitrocellulose*, **38**, 147 (1943) [C. A., **38**, 2210 (1944)]; *ibid.*, **38**, 125 (1943) [C. A., **38**, 2823 (1944)].