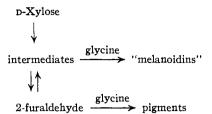
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as when 2-furaldehyde is reacted with a large excess of glycine. 2-Furaldehyde is undoubtedly a member of a complex system of the type shown



It is probable that the small amount of 2furaldehyde 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 pro-

cedures were used.

Procedure 1.—A mixture of 3.7 g. (0.025 mole) of p-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 prod-uct of the Central Scientific Co., Chicago, III.) and di-alyzed 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-

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

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 for the back of $f_{\rm exp}$ is the back of $f_{\rm exp}$. 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 1). 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 p-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 p-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 Dxylose-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.

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

Columbus, Ohio

RECEIVED APRIL 3, 1950

[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 coworkers published two papers' dealing with the oxidation of propionate by alkaline permanganate. They elucidated the mechanism of this reaction by means of C^{11} , a radioactive isotope of carbon of short half-life, and the only radiocarbon tracer

(1) The experimental work reported in this communication was cairied 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

$$CH_3CH_2C^*O_2^- + 4MnO_4^- = C_2^*O_4^- + C_2^*O_4^-$$

 $C^{*}O_{3}^{-} + 4MnO_{2} + 2H_{2}O + OH^{-}$

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 seission 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- $2-C^{14}$, 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 imend of this period the hasks were durckly chilled by in-mersion in cracked ice. Excess permanganate was de-stroyed with hydrogen peroxide and the manganese dioxide removed by centrifugation. The precipitate was then washed several times with boiling water.³ The superna-tant and washings were diluted to 200,00 ml. This solu-tion was then split into two equal fractions. Fraction 1 was acidified with acetic acid, calcium acetate was added the calcium avolate precipitated the mixture

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 discussed solved 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 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 dep-osition cup for solids,⁸ and employing 0.100 ml. micro-pipets 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
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OX1DATION OF PROPIONATE-1-C14 WITH ALKALINE PER-MANGANATE

		ALD	
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 $\pm 2\%$. 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 = $0.98 \pm 2\%$.

(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.

the oxalate/carbonate ratio is indeed equal to one, confirming the results of McNair⁹ and of Nahinsky *et al.*¹ The data quoted constitute the mean of three separate runs for the chemical analyses and of two separate experiments employing radioactive carbon, for the radioactivity data. The standard deviations are of the magnitude shown.

Our results are compared to those obtained with C^{11} in Table II. At first glance it would indeed appear that a significant isotope effect can be observed if C^{14} is substituted for C^{11} in this particular reaction. Certain doubts as to this conclusion can be raised, however. The inherent error in our determinations is probably of the order of magnitude indicated. The deviations in the earlier work are about 8% for the

carbonate fraction, on the basis of the published data, based on two separate runs. No statement as to the magnitude of the total error involved in the estimation of the radioactivity is made. In view of the early date of the investiga-

TABLE II

Comparison of Data for C¹¹ and C¹⁴ Labeled Acids

	CH3- CH2C ¹¹ O2	CH3- CH2C ¹⁴ O2 -
Per cent. activity in CO ₃ =	13.1	10.4
Per cent. activity in $C_2O_4^-$	86.9	90.0
$\alpha C - \beta C$ rupture/ $\alpha C - CO_2^-$ rupture	6.6	8.9

tion and the information quoted as to counting procedure used, it is reasonable to assume that this error too is at least of the same order of magnitude. Assuming, for a moment, a counting error of about 5% (*i. e.*, inherent counting error and corrections due to self-absorption, back-scattering, etc.) in the activity, say, of the oxalate fraction, it becomes apparent that this might raise the C¹¹

TABLE III

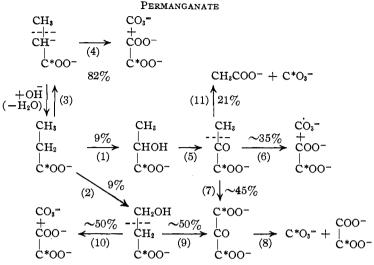
Oxidation of Pyruvate-2-C¹⁴ with Alkaline Permanganate

Compound	Mmole found or added	Carbon m. equiva- lents	Cts./min.	Relative molal specific activity
Pyruvate	0.587	1.760	56800	100
Oxalate	. 500	1.00	45800	95
Carbonate	.618	0.618	800	<1
Acetate	.103	0.206	9750	100
Σ products		1.824	56350	

All analytical and counting data $\pm 2\%$. Conditions of the experiment: 1 ml. of 0.5867 *M* solution of pyruvate incorporating 56,800 cts./min. Other details similar to those in Table I. Carbon m. equivalents = mmoles × number of carbon atoms/molecule. Found: (oxalate + acetate)/carbonate = 603/618 = 0.935. Decarboxylation/ oxidation = 9750/45,800 = 0.212.

(9) B. McNair, THIS JOURNAL, 54, 3249 (1932).

TABLE IV TENTATIVE FORMULATION OF PROPIONATE OXIDATION BY ALKALINE



values to those found by us. Thus there may not exist any real difference even in the rupture ratios. In any event the isotope effect for the $C^{14}-C^{11}$ pair, for the reaction studied, if present at all, must be equal to or less than five per cent. It might be possible to re-examine the problem using the $C^{14}-C^{13}$ pair and thus to settle the question definitely.

Oxidations of Pyruvate-2-C¹⁴.—Our results are summarized in Table III.

The limits of uncertainty are of the same size as in the previous experiments. Although the ratio, two carbon compounds/carbonate, is slightly lower than the one predicted by theory, all the activity is accounted for. Comparison of the relative specific activities shows that (a) *all* the acetate must have arisen by decarboxylation and that (b) *none* of the carbonate had its origin in the carbonyl carbon of the pyruvate. This result is in agreement with the data of Calvin and Lemmon on ethyl pyruvate.¹⁰

These results, in combination with the ratio of activities, lead us to the conclusion that decarboxylation before oxidation must have taken place in approximately 21% of the total number of pyruvate molecules. This reaction had not been taken into consideration by the original investigators of the propionate oxidation. The correction which must be introduced when discussing the propionate reaction is small, however. Table IV summarizes our findings on propionate and pyruvate, as well as those of the earlier investigators on propionate, lactate and β -hydroxypropionate. From this it can be shown that only about 9% of all propionate molecules go through the pyruvate stage. Thus only 1.8% of the propionate is oxidized to acetate plus carbonate. This is below the limits of the experimental accuracy of either Nahinsky's or our investigations.

(10) M. Calvin and R. Lemmon, ibid., 69, 1232 (1947).

Summary

1. Comparison of results obtained for the alkaline permanganate oxidation of propionate-1-C¹⁴ with those for the corresponding C¹¹ 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. 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.

2. Since pyruvate has been postulated as an

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

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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

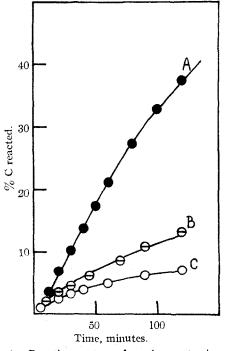


Fig. 1.—Reaction rates of carbon-potassium perchlorate (1:0.5 mole) mixtures at 367°: A, standard sample, mixed, wetted and pressed at 600 atm.; B, same mixture, ground together but not pressed; C, mixed by shaking only. temperature of initiation has been observed,⁸ and although no information is available 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 $320-385^{\circ}$, it reacted according to the equation $KCIO_4 + 2C = 2CO_2 + KCI$. 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 600 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

⁽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)]; Hertjes 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)].