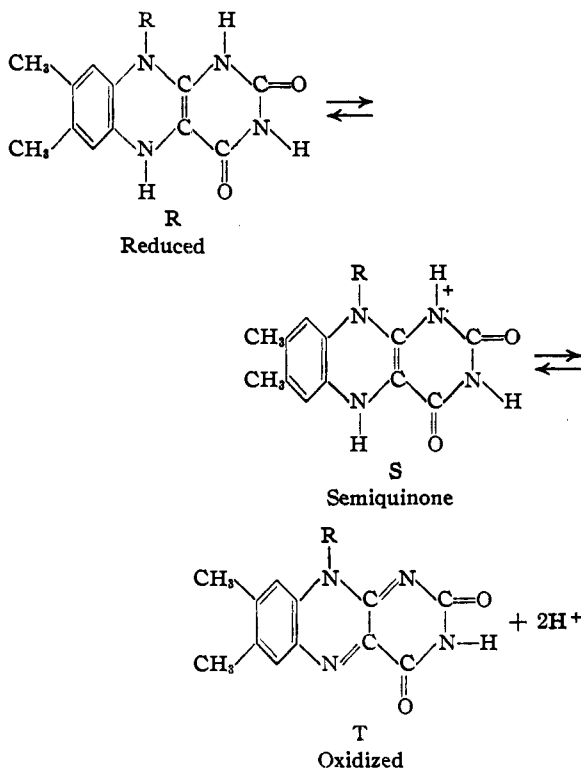


that reacts with oxygen can stabilize itself in the oxidized state by a bond rearrangement, *i. e.*, there is no necessity of proposing the formation of organic peroxides. For example, riboflavin nucleotides are the prosthetic groups of the flavo (yellow) enzymes. Let R represent the ribose group, the phosphate linkage, and the adenine group.



On oxidation, the bonds rearrange similarly to the rearrangement for the semiquinone mechanism.

It is probable that even the oxidases that reduce oxygen to water do not form organic peroxides. Formation of enzyme peroxide probably leads to inactivation of the enzyme. Ionization preceding or following the oxidation adequately explains the hydrogen balance without introducing the idea of atomic hydrogen exchange (Wieland's dehydrogenation theory). Certainly in aqueous solution at the pH of normal cell activity there is an adequate supply of hydrogen ions to give instantaneous exchange.

LuValle and Goddard<sup>7</sup> have suggested that electron donor and electron acceptor are bound in a complex and that reaction takes place by the semiquinone mechanism. Either the donor or acceptor may combine with the enzyme, followed by a univalent oxidation-reduction, and this enzyme-semiquinone complex will then react with the other reactant to form the final products. By this mechanism the semiquinones are never free in the solution; they only exist bound to the enzyme. It is shown that the semiquinone mechanism can explain the observed kinetics for many respiratory enzymes. This mechanism does not involve bound peroxide formation or exchange of hydrogen atoms. Chain mechanisms are not necessary to explain the observed data.

#### Summary

The chain peroxide mechanism of autoxidation is briefly compared with the semiquinone mechanism. It is pointed out that the coenzymes involved in biological oxidation-reductions are much more likely to undergo reaction with oxygen *via* the semiquinone mechanism than by the chain, bound peroxide mechanism.

(7) LuValle and Goddard, in publication, "Quarterly Review of Biology."

ROCHESTER 4, N. Y.

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CONTRIBUTION FROM THE RADIATION LABORATORY AND DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA

## Preparation of 1-C<sup>14</sup>-Propene-1 and the Mechanism of Permanganate Oxidation of Propene<sup>1</sup>

BY B. A. FRIES<sup>2</sup> AND M. CALVIN

The preparation of 1-C<sup>14</sup>-propene-1 was undertaken in order to have available propene labelled in a terminal position and, incidentally, to study the stability of the double bond to migration when preparing propene under a variety of conditions. During the course of this investigation, a reliable procedure for the degradative analysis of the propene had to be developed. This analytical prob-

(1) This paper is based on work performed under Contract Number W-7405-eng-48 with the Atomic Energy Commission in connection with the Radiation Laboratory of the University of California, Berkeley, California.

(2) While on leave California Research Corporation, Richmond, California.

lem led to a study of the oxidative degradation of propene with permanganate.

A number of methods were available for the preparation of propene. Several of these methods were tried with C<sup>14</sup> labelled materials, while others were discarded when preliminary tests with non-radioactive materials indicated either very poor yields or impure products. The first three of the following methods were actually employed for radioactive propene synthesis: (1) dehydration of *n*-propanol with metaphosphoric acid, (2) dehydration of *n*-propanol over heated alumina, (3) pyrolysis of *n*-propyltrimethylammonium hy-

dioxide, (4) pyrolysis of methyl *n*-propyl xanthate, and (5) dehydrobromination of *n*-propyl bromide with alcoholic potassium hydroxide. Extensive rearrangement of the double bond was found to occur when preparing propene by dehydration with metaphosphoric acid and with heated aluminum oxide. However, the pyrolysis of the quaternary ammonium base gave little, if any, rearrangement and the product consisted principally of 1-C<sup>14</sup>-propene-1 (CH<sub>3</sub>-CH=CH<sub>2</sub>), whereas in the other cases, mixtures of 1-C<sup>14</sup>-propene-1 and 3-C<sup>14</sup>-propene-1 (CH<sub>3</sub>-CH=CH<sub>2</sub>) were obtained.

**Degradation Procedure. Permanganate Oxidation of Propene.**—A number of procedures were available for the analysis of the labelled propene, including oxidative degradation with permanganate or dichromate, ozonolysis and glycol formation with hydrogen peroxide, acetyl peroxide or Prévost reagent, and subsequent oxidation and splitting of the glycol with periodate. Ozonolysis of propene gives rise to a mixture of formaldehyde and acetaldehyde, which are not too easily separated. Preliminary glycol formation and periodate oxidation also yields these same two aldehydes and in addition involves more manipulation. Acid permanganate oxidation should produce acetic and carbonic acids if propylene glycol is an intermediate. This appeared to be a satisfactory procedure, particularly since Evans<sup>3</sup> reported that propylene glycol was converted quantitatively to acetic acid and carbon dioxide with neutral permanganate at 50°, although in the presence of alkali, oxalic acid was formed. Hence, examination of the acetic and carbonic acids for C<sup>14</sup> should indicate the extent of labelling of the two terminal carbon atoms of the propene. However, rearrangement of the double bond might also occur during the analysis, but this could not be determined until some radioactive propene had been prepared. Although permanganate oxidation was chosen for the degradative analysis, in one instance ozonolysis was employed to confirm the results of the permanganate method.

The following procedure was first tested with non-radioactive propene. Approximately three millimoles of propene was introduced into an evacuated 3-necked flask of about 385 ml. volume. Fifty ml. of water or buffer solution was added through a dropping funnel. An induction stirrer<sup>4</sup> was used to agitate the aqueous phase. An amount of 0.4 *N* potassium permanganate calculated to be just sufficient to oxidize propene to propylene glycol was added over a period of forty-five minutes. This was followed by the addition of 110% of the amount of 2 *N* potassium permanganate required for the oxidation of propylene glycol to acetic and carbonic acids. This addition required forty-five minutes, after which the solution

was stirred fifteen minutes more. A sulfuric acid-acidified solution of ferrous sulfate was added to reduce all manganese to the manganous state and simultaneously liberate carbon dioxide. The flask was connected to a sodium hydroxide absorber and swept with nitrogen gas to collect this carbon dioxide fraction. The solution remaining was steam distilled to recover acetic acid. This latter was titrated with sodium hydroxide and evaporated to dryness as sodium acetate. The weight of the salt obtained and its subsequent combustion to carbon dioxide when compared with the titration value indicated that the salt was the acetate. This procedure was studied at several values of *pH* and at two temperatures. The results are shown in Table I.

TABLE I  
OXIDATION OF PROPENE WITH POTASSIUM PERMANGANATE  
AT SEVERAL VALUES OF *pH*

Starting solution	0.04 <i>N</i> NaOH	0.02 <i>N</i> NaOH	0.1 <i>M</i> PO <sub>4</sub> <sup>3-</sup> <i>pH</i> 7.4	Dis-tilled water	0.1 <i>M</i> PO <sub>4</sub> <sup>3-</sup> <i>pH</i> 6.0	0.1 <i>M</i> PO <sub>4</sub> <sup>3-</sup> <i>pH</i> 4.0
Temp., °C.	35	35	35	35	25	25
Moles CO <sub>2</sub> /moles C <sub>3</sub> H <sub>6</sub>	1.54	1.31	1.28	1.11	0.94	0.94
Moles acetic acid/moles C <sub>3</sub> H <sub>6</sub>	0.18	0.38	0.46	0.57	0.73	0.70
Acetic acid/CO <sub>2</sub>	0.11	0.29	0.36	0.51	0.78	0.75

It can be seen that in weak acid solution about 70% of the theoretical amount of acetic acid and 90% of the theoretical amount of carbonic acid may be recovered. This calculation was based on the splitting of propene at the double bond to yield equimolar amounts of acetic and carbonic acids. There was no significant change in yield of these two fractions on decreasing the *pH* from 6 to 4 and stronger acid was avoided to reduce the possibility of a shift of the double bond in propene during the analysis. In the subsequent use of this procedure with the various samples of radioactive propene, the reaction was carried out at *pH* 4 and at room temperature. Inasmuch as the total carbon recovery in the carbon dioxide and acetic acid fractions was quite low (70–80%) an attempt was made to locate the missing carbon. The solution remaining after steam distillation of the acetic acid was made 6 *N* in sulfuric acid and 0.5 *M* in chromic oxide, heated to boiling and swept with oxygen for one hour. Considerable carbon and C<sup>14</sup> activity was found in this fraction. The inclusion of this additional carbon boosted the total carbon recovery to 85–95%.

There were several indications that this oxidizable residue was oxalic acid. First, oxalic acid may be found during alkaline permanganate oxidation of propylene glycol.<sup>3</sup> Second, oxalic acid is oxidized very slowly at 25° and *pH* 4 by potassium permanganate or manganese dioxide and therefore, the oxalic acid would be stable, if present. Third, the nature of the analytical procedure eliminated the possibility of a one carbon compound, since these compounds (methyl alco-

(3) W. L. Evans, *THIS JOURNAL*, **45**, 171 (1923).

(4) W. G. Dauben, J. C. Reid and P. E. Yankwich, *Anal. Chem.*, **19**, 828 (1947).

hol, formaldehyde, formic acid), if not completely oxidized by the permanganate, would be volatilized during the steam distillation. In addition, subsequent specific activity determinations of this fraction (see Discussion) eliminated the possibility of a three carbon compound and corresponded well with a two-carbon substance. Hence, this residue was either oxalic, glycolic or glyoxylic acid. The last two of these may be intermediates in the formation of oxalic acid. Ethylene glycol also satisfies the chemical properties set for the residue, but it is difficult to see why this glycol should remain unoxidized while propylene glycol, a probable intermediate in the above oxidation, is apparently completely reacted.

In one experiment with radioactive propene, the isolation of oxalic acid was attempted. After the addition of the last permanganate, all manganese was removed as manganese dioxide by centrifugation. Inactive sodium oxalate was added as a carrier and the oxalate was ultimately precipitated as calcium oxalate after separation from phosphate by employing the scheme of Swift.<sup>5</sup> The completeness of recovery of oxalate could not be accurately determined, but appeared to be nearly quantitative. However, since the calcium salts of glycolic and glyoxylic acid are relatively insoluble, they might have been carried down with the calcium oxalate if present. The calcium oxalate was titrated with permanganate in the usual manner, and the carbon dioxide was collected and analyzed for C<sup>14</sup> activity. The titration agreed within 3% with the formula calcium oxalate for the calcium precipitate; however, since the amount of carrier was about four times the amount of oxalate expected, the presence of other insoluble calcium salts might have been masked. The amount of C<sup>14</sup> found as oxalate was about 70% of the amount found by direct chromic oxide oxidation of the residue in another experiment using radioactive propene from the same preparation.

**Ozonolysis Method.**—A highly refined procedure was not developed but the following scheme gave a satisfactory check with the result of the acid permanganate oxidation. About three millimoles of propene was transferred to the ozonolysis vessel, 15 ml. of ethyl chloride was added and the vessel immersed in a Dry Ice-acetone-bath. A current of oxygen containing 2-3% ozone was bubbled through the solution until the solution turned blue (indicating excess ozone). The vessel and contents were warmed to 0°, 10 ml. of water added and shaken with the ethyl chloride. The ethyl chloride was removed by evaporation under house vacuum. The aqueous solution, which now contained formaldehyde and acetaldehyde, was made alkaline with sodium hydroxide. Excess potassium permanganate was added and the solution heated to 50°. The formaldehyde was oxidized to carbon dioxide while the acetaldehyde was oxidized to acetic acid. From this point on, the analysis was carried out in the same manner as the permanganate procedure. In this ozonization some propene probably was swept out of the solution by the current of oxygen, while some of the aldehydes were lost during the evaporation of ethyl chloride. In addition some ethyl chloride remained in the aqueous phase and was oxidized to acetic acid. Although the total carbon

recovery was high and C<sup>14</sup> recovery was low, the distribution of C<sup>14</sup> should not be affected.

**Preparation of 1-C<sup>14</sup>-*n*-Propanol (CH<sub>3</sub>-CH<sub>2</sub>-<sup>14</sup>CH<sub>2</sub>OH).**—The principal intermediate in the synthesis of propene was *n*-propanol. The starting point of this synthesis was barium carbonate containing C<sup>14</sup>. Ethylmagnesium bromide was carbonated with the C<sup>14</sup>O<sub>2</sub> obtained from 21 millimoles of barium carbonate containing approximately 800 microcuries of C<sup>14</sup>. A vacuum line technique (4) was employed. Solid sodium propionate was recovered in 95% yield. A very high specific activity product was not required in this experiment and a large dilution of C<sup>14</sup> activity could be tolerated. Consequently, the reduction of the acid to alcohol was carried out on the *n*-propyl ester. The use of this ester eliminated the subsequent separation of two alcohols following the hydrogenation. The esterification was carried out on a 40 millimole scale by adding inactive sodium propionate to 1.62 g. (16.8 millimoles) of the radioactive salt. The esterification was driven to completion by azeotropic distillation. The solid salt was refluxed for several hours with a mixture of 9.0 ml. of *n*-propyl alcohol, 10.0 ml. of benzene and 1.1 ml. of concentrated sulfuric acid. Water was removed as the ternary azeotrope (68.5°) with *n*-propyl alcohol and benzene. A 16-inch, 6-mm. i. d., vacuum-jacketed, unpacked column was used for the distillation. When the temperature of the distillate reached 74°, the flask was cooled and 1.0 g. of calcium carbonate was added to destroy excess sulfuric acid. The distillation was continued, the remaining benzene being removed as the binary azeotrope (77.1°) with *n*-propyl alcohol. The distillation was stopped when the temperature reached 92°. The ester-alcohol solution remaining was removed from the calcium sulfate-calcium carbonate residue by vacuum transfer. This solution, about 8 ml. was pipetted into a high pressure hydrogenation bomb (Aminco, 43 ml. size) containing 2.0 g. of copper chromite catalyst (Adkins). The bomb was charged with 2500 p. s. i. of hydrogen, heated to 250° and maintained there for nine hours. The contents of the bomb were transferred on the vacuum line into a flask containing calcium oxide where the alcohol was dried. The alcohol was again transferred on the vacuum line into a small distilling flask and fractionally distilled using the column described above. The fraction boiling from 96-97° was recovered. The fraction boiling below 96° (about 2 ml.) was returned to the distilling flask with 2.5 ml. of *n*-propyl alcohol and the mixture redistilled. This was repeated again with 2.0 ml. of *n*-propyl alcohol. The 96-97° fractions were combined with the first fraction collected. In this manner 10.3 ml. of 1-C<sup>14</sup>-*n*-propyl alcohol was obtained. The individual steps in the above procedure were tested first with inactive materials. These tests gave yields of 90-95% for the carbonation of ethylmagnesium bromide and 95% for the esterification and hydrogenation when measured by saponification. In the radioactive synthesis, the carbonation yield was 95%. The chemical yields of the other steps were not checked because the amount of alcohol which remained with the ester after azeotropic distillation was not known. About 80% of the starting C<sup>14</sup> was recovered in the final product, which contained  $4.58 \times 10^6$  c./min./ml. or about 50  $\mu$ c./ml.

**Preparation of 1-C<sup>14</sup>-*n*-Propyl Bromide.**—Propyl bromide was prepared from *n*-propanol by the phosphorus and bromide method,<sup>6</sup> but additional phosphorus and bromine were added. The yield of propyl bromide was 76% based on propanol. A low C<sup>14</sup> activity sample of propanol was prepared by dilution of the high activity material for use in this preparation.

**Dehydration of *n*-Propanol with Metaphosphoric Acid.**—A 2-ml. sample of propanol containing 6350 c./m. C<sup>14</sup> per millimole of alcohol (prepared by dilution of the high activity product) was dehydrated to propene by dropwise addition of the alcohol to 3 ml. of metaphosphoric acid at 250° according to the method of Newth.<sup>7</sup> Water and

(5) E. H. Swift, "A System of Chemical Analysis," Prentice-Hall, Inc., New York, 1904, p. 469, *et seq.*

(6) A. H. Blatt, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 37.

(7) G. S. Newth, *J. Chem. Soc.*, **79**, 915 (1901).

alcohol were condensed in a trap at  $-20^{\circ}$  while the propene was passed through Drierite, then condensed in a Dry Ice trap. Considerable alcohol distilled out of the flask without reacting and the yield of propene was 40% based on the starting propanol. The gas sample was analyzed by mass spectrometer.<sup>7a</sup> The analysis of the gas showed 80% propene, 9% butenes, 9% butanes and pentanes and 1% pentenes and hexenes. The propanol was analyzed by mass spectrometer and found to be 99.5% pure; the impurity may have been butyl alcohol.

**Dehydration of *n*-Propanol over Heated Aluminum Oxide.**—A 2-ml. portion of the above dilute propanol was dehydrated by dropwise addition over a period of thirty minutes into a vertically mounted quartz furnace tube containing aluminum oxide at  $390^{\circ}$ . The aluminum oxide was 12–24 mesh Alorco Alumina (Aluminum Company of America, Grade F-1) packed in a bed 23 cm. long and 0.7 cm. in diameter. Traps were arranged as in the previous experiment. Continuous nitrogen sweeping was maintained to reduce the residence time in the catalyst. The contact time was approximately 5 seconds. A second sample of alcohol was dehydrated over laboratory prepared aluminum oxide obtained by precipitation of aluminum hydroxide from reagent grade aluminum nitrate. The catalyst temperature was  $415^{\circ}$  while the contact time was only 2 seconds. The analysis of the first of these gas samples was 97% propene and 3% butenes, while the second gas sample contained 95% propene, 3.5% butenes, 0.5% propane and 0.5% *n*-butane. The yield of propene was about 95% in both cases.

**Pyrolysis of *n*-Propyltrimethylammonium Hydroxide.**—The quaternary ammonium bromide was prepared by the addition of 5 ml. of *n*-propyl bromide (containing 8300 c./m.  $C^{14}$ /millimole) to excess  $(CH_3)_3N$  in alcohol and refluxing for several hours. The solvent was evaporated, the bromide dissolved in water and excess freshly prepared silver oxide was added to convert the bromide to hydroxide. After filtering silver bromide and excess silver oxide the aqueous solution was boiled to dryness in a system containing a cold water condenser, a 1 *N* hydrochloric acid wash bottle to remove  $(CH_3)_3N$ , a tube of Drierite and a liquid nitrogen trap to condense propene. The system was swept with nitrogen during the heating. The yield of propene was approximately 90%. Analysis of the gas showed 99% propene, 0.5% butenes and 0.5% ethylene.

**Pyrolysis of Methyl *n*-Propyl Xanthate.**—The procedure of Schurmann and Boord<sup>8</sup> was employed for preparing the xanthate ester, however, the final ester was not purified by vacuum distillation as carried out by these authors. The decomposition of the ester took place very slowly and after boiling for twenty-four hours, only half the ester was decomposed. The slow decomposition of primary xanthates was observed by Whitmore and Simpson.<sup>9</sup> The system was swept with a slow current of nitrogen and the gases were passed through a 1 *N* sodium hydroxide wash bottle to remove COS and  $CH_3SH$ , then through a drying tube and finally into a liquid nitrogen trap. The yield of propene was about 25% and the gas composition was 56% propene, 38% butenes, 1.4% ethene, 14% COS while the remainder of the gas consisted of several sulfides and mercaptans. This method of propene preparation, besides giving a gas difficult to free of sulfur compounds also contained an extraordinarily large amount of butene. The use of this method was not attempted with radioactive propanol.

**Dehydrobromination of *n*-Propyl Bromide with Alcoholic Potassium Hydroxide.**—Propene was prepared by refluxing the bromide with excess potassium hydroxide dissolved in absolute ethanol in a system similar to those

described above. The yield of propene was about 10%, the bulk of the product being ethyl propyl ether. Nef<sup>10</sup> reported a yield of 20% propene. Analysis of the gas sample showed 75% propene, 16% butenes, 3% isobutane, 3% ethyl propyl ether and traces of ethane, propane and propyl bromide. The use of this method was not attempted with radioactive propyl bromide.

**Radioactivity Determination.**—The procedures developed by Dauben, Reid and Yankwich<sup>4</sup> were employed for sample preparation and counting.

## Results and Discussion

In Table II a summary of the results of the permanganate degradations of the various samples of propene is presented. Since the mechanism of permanganate oxidation of propene, the reliability of this oxidation as an analytical procedure, and the nature of the labelling of the propene could not be determined independently, it was necessary to examine the data from these three points of view. The fact that different specific activities were found in the various fractions from propene prepared by different methods proved that rearrangement of the double bond to the equilibrium mixture did not occur during the analysis. Inspection of experiments 1, 2, and 3 showed that extensive migration of the double bond occurred during the preparation by these methods and, in fact, the propene produced in experiments 1 and 3 consisted of equilibrium mixtures of 1- $C^{14}$ -propene-1 and 3- $C^{14}$ -propene-1. However, the propene derived from the quaternary ammonium base (experiment 4) showed little, if any, rearrangement of the double bond and the product consisted, almost entirely, of 1- $C^{14}$ -propene-1.

The mechanism which has been assumed for the oxidative splitting of olefins with permanganate consists of rupture of the molecule at the site of the double bond with the production of acetic and carbonic acids in the case of propene. If the acetic acid was to be used as a measure of labelling of the methyl group of propene, it was necessary to demonstrate that all the  $C^{14}$  activity was present in the methyl group of the acetic acid. Therefore in the pyrolysis of a sample of barium acetate to acetone and barium carbonate, the latter should contain no  $C^{14}$ . A sample of acetate from experiment 2, when pyrolyzed, showed that 5% of the  $C^{14}$  present was present in the carboxyl group. The pyrolysis of a sample of synthetic methyl-labelled acetate<sup>11</sup> yielded 1.5–2% of the total activity in the barium carbonate which would correspond to 3–4% of the activity apparently present in the carboxyl group. Hence, the above result may be taken to mean that little, if any, carboxyl activity was present and that the carboxyl group of the acetate was derived solely from the central carbon atom of the propene. Therefore, in every case shown in Table II, the specific activity of the methyl carbon of acetic acid may be obtained by doubling the specific activity shown for acetic acid. If acetic acid is obtained only from splitting of propene at the double bond, then

(7a) All gas samples were analyzed by mass spectrometer by Dr. N. Bauer, through the courtesy of California Research Corporation, Richmond, California.

(8) I. Schurmann and C. E. Boord, *THIS JOURNAL*, **55**, 4930 (1933).

(9) F. C. Whitmore and C. T. Simpson, *ibid.*, **55**, 3809 (1933).

(10) J. U. Nef, *Ann.*, **309**, 126 (1899).

(11) S. Aronoff, V. Haas, B. A. Fries, to be published.

TABLE II  
 ACID PERMANGANATE ANALYSES OF PROPENE SAMPLES

Preparative procedure	Expt. 1 Dehydration with metaphosphoric acid			Expt. 2 Dehydration with Alorco aluminum oxide			Expt. 3 Dehydration with laboratory-prepared aluminum oxide			Expt. 4 Pyrolysis of n-propyltrimethylammonium hydroxide		
	Carbon dioxide	6350 Acetic acid	Oxalic acid	Carbon dioxide	6350 Acetic acid	Oxalic acid	Carbon dioxide	6350 Acetic acid	Oxalic acid	Carbon dioxide	8300 Acetic acid	Oxalic acid
Specific activity of C <sup>14</sup> in starting material (c./m./millimole of C <sub>3</sub> H <sub>6</sub> )												
Fraction analyzed												
Specific activity of C <sup>14</sup> in fraction (c./m./millimole C)	2790	1610	1560	3980	1100	2130	2840	1530	2020	7600	130	3810
% of total C <sup>14</sup> recovered in fraction <sup>a</sup>	41	42	5.0	59	24	5.9	38	39	6.2	91	2.2	5.7
Moles/mole C <sub>3</sub> H <sub>6</sub>	0.94	0.83	0.10	0.94	0.70	0.09	0.85	0.81	0.10	1.0	0.71	0.07
Total C <sup>14</sup> recovery		88			89			83			99	
Total C recovery		94			84			89			85	

<sup>a</sup> In this calculation only the olefin content of the gas sample used in the potassium permanganate analyses was taken into account. The presence of labelled butene and other olefins derived from the original labelled propanol introduces some error in the calculation of yields as well as in the specific activity of the various fractions. This error cannot be corrected, since neither the number of C<sup>14</sup> labelled atoms per molecule nor the isomers were known.

a case in which there was no activity in the acetate fraction would prove that all the C<sup>14</sup> was in the methylene carbon of the propene. This was the case in experiment 4 where only 3% of the C<sup>14</sup> activity was present in the acetate. This particular propene sample was checked by the ozonization analysis previously described and no activity could be found in the acetate. Therefore, the propene produced in experiment 4 consisted of the isomer 1-C<sup>14</sup>-propene-1 to the extent of 97–100%. This result also demonstrated that acetic acid can arise only from the CH<sub>3</sub>—CH= portion of the molecule. Accordingly, acetate was the most reliable indicator of the activity of the CH<sub>3</sub>— position in propene and this was true even though acetic acid was not recovered in 100% yield.

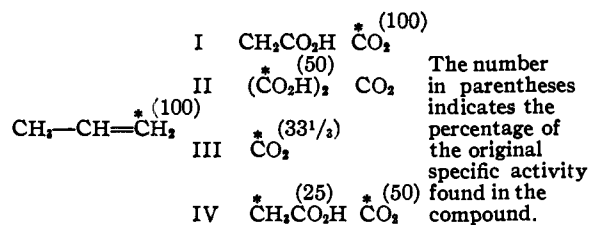
The specific activity of the carbon dioxide fraction always was found to be lower than that calculated on the basis of the specific activity of the acetate. Thus, in experiment 1, the specific activity of the starting propanol was 6350 c./m. per millimole. Since all the C<sup>14</sup> was located in the 1-position in the propanol, the specific activity of this particular carbon atom was also 6350 c./m. per millimole of carbon. The specific activity of the methylene carbon of the propene produced in experiment 1 was, therefore, 6350 — (2 × 1610) = 3130 c./m. per millimole C, but the specific activity found in the carbon dioxide fraction was only 2790 c./m. In experiment 2 the results were similarly 4150 c./m. *versus* 3980 c./m.; in experiment 4, 8040 c./m. *versus* 7600 c./m. These data indicated that the carbon dioxide-carbon was not derived exclusively from the methylene carbon, but probably from the methyl and central carbon atoms as well to a small extent.

Examination of the oxalic acid fraction revealed that the oxalate contained the methylene carbon atom of propene. The possibility of one carbon compounds being present in this residue has been considered already and has been eliminated on the basis of oxidation and volatility. The possibility that relatively large amounts of some three carbon

compounds might be present may be eliminated on the basis of the specific activity of the fractions. If this oxidizable residue were entirely a three carbon compound, the specific activity in the active position would be three times the value shown in Table II. In experiment 4, the specific activity reported, when multiplied by three would give a result much higher than the original specific activity present in the starting material. On the other hand, if the substance were a two carbon compound, the specific activity in the labelled position corresponded closely to that known to be present in the methylene carbon. These results demonstrated that some propene was split at the CH<sub>3</sub>—CH bond, perhaps to the extent of 15–20%. The —CH=CH<sub>2</sub> group was oxidized to oxalic acid, while the CH<sub>3</sub>-group was split off as a one carbon compound, presumably oxidized to carbon dioxide, although some may not have been oxidized beyond methanol or formaldehyde. These last two compounds would not be recovered in the analytical procedure and this may account for the incomplete recovery of C<sup>14</sup> and total carbon. The specific activity of C<sup>14</sup> in the carbon dioxide fraction (representing the =CH<sub>2</sub> group) was therefore low due to the carbon dioxide which arose from the methyl group and probably from the central carbon atom as well.

In the alkaline oxidation of propylene glycol,<sup>8</sup> the yield of carbon dioxide was over one mole per mole of glycol, while acetate was lower and oxalate higher than that obtained from the acid oxidation. This led to the performance of an alkaline oxidation on propene from experiment 4. The oxidation was carried out in the same manner as those previously described except that the medium was 0.04 N in sodium hydroxide. The number of moles of carbon dioxide, acetic acid, and oxalic acid obtained per mole of propene were 1.64, 0.33, and 0.16, respectively. The specific activities of these three fractions were, respectively, 3410, 560, and 4370 c./m. per millimole of carbon. The yield of carbon dioxide was very high and its spe-

cific activity was very low, indicating that a considerable portion of it had come from carbon atoms other than the methylene group of the propene. Quantitative estimates, based upon relative yields and specific activities, indicated that nearly half of the propene had been completely oxidized to carbon dioxide, the remainder going partly ( $1/3$ ) to acetic acid and carbon dioxide and partly ( $1/6$ ) to oxalic acid and carbon dioxide. Still another route of oxidation was required to account for the small amount of activity found in the acetate fraction. This could be accounted for by some symmetrical intermediate (retaining the methyl group) such as isopropyl alcohol or acetone. There are three, and probably four, paths through which propene may be oxidized by permanganate. In the acid oxidation, path I predominates ( $5/6$ ) with paths II and III contributing minor and approximately equal parts. Somewhat similar conclu-



sions were deduced for the alkaline permanganate oxidation of propionic acid by Nahinsky and Ruben.<sup>12</sup>

On the basis of the acetic acid specific activity, the propene prepared with metaphosphoric acid was a 50–50 equilibrium mixture of the two forms of labelled propene, the propene prepared from commercial aluminum oxide was 65% 1-C<sup>14</sup>-propene-1 and 35% 3-C<sup>14</sup>-propene-1, the propene prepared from the laboratory alumina was approximately a 50–50 equilibrium mixture; while the propene derived from the quaternary ammonium hydroxide was 97% 1-C<sup>14</sup>-propene-1 and 3% 3-C<sup>14</sup>-propene-1.

Isomerization during olefin preparation by dehydration reactions has been reported frequently,<sup>13–16</sup> while many cases have been reported where little or no isomerization occurred.<sup>17–20</sup> Asinger<sup>13</sup> found general isomerization of the double

(12) P. Nahinsky and S. Ruben, *THIS JOURNAL*, **63**, 2275 (1941).

(13) F. Asinger, *Ber.*, **75B**, 1247 (1942).

(14) C. Matignon, H. Moureau and M. Dode, *Compt. rend.*, **196**, 973 (1933).

(15) G. Egloff, J. C. Morell, C. L. Thomas and H. S. Bloch, *THIS JOURNAL*, **61**, 3571 (1939).

(16) G. T. Morgan and W. J. Hickingbottom, *J. Chem. Soc., Trans.*, **73**, 97 (1923).

(17) H. Pines, *THIS JOURNAL*, **65**, 3892 (1933).

(18) W. G. Appleby, C. J. Dobratz and S. W. Kapranos, *ibid.*, **66**, 1938 (1944).

(19) V. I. Komarevsky, S. C. Uhlick and M. J. Murray, *ibid.*, **67**, 557 (1945).

(20) A. L. Henne and A. F. Matuszak, *ibid.*, **66**, 1649 (1944).

bond all along the carbon chain when dodecanol was dehydrated over alumina at 370–380° or with metaphosphoric acid. Isomerization was observed with alumina at temperatures as low as 250° where the dehydration reaction was incomplete. Pines<sup>17</sup> obtained only butene-1 when dehydrating *n*-butanol over alumina although Matignon, Moureau, and Dode<sup>14</sup> reported 15% butene-2 when using pure alumina and 90% with impure alumina. Pines believed the isomerization reported by Matignon occurred during analysis. Appleby, Dobratz and Kapranos<sup>18</sup> and Komarevsky, Uhlick and Murray<sup>19</sup> employing spectroscopic examination found no isomerization during the dehydration of primary hexanol, heptanol and octanol over alumina. Ewell and Hardy<sup>21</sup> studied the isomerization of pentenes over alumina and showed that the reaction required several hours to come to equilibrium. In the present study dehydration of *n*-propanol with alumina or phosphoric acid resulted in complete equilibration of the two isomeric forms. The ease of isomerization may be due to the symmetrical structure of propene.

Pyrolysis of *n*-propyltrimethylammonium hydroxide gave essentially pure 1-C<sup>14</sup>-propene-1 in 90% yield. A side reaction of this pyrolysis results in the formation of methanol and a mixed tertiary amine. von Braun<sup>22</sup> found 5–10% methanol while Hanhart and Ingold<sup>23</sup> and Ingold and Vass<sup>24</sup> obtained 16–19% methanol on pyrolysis of the above quaternary base. The yield of propene in the present experiment falls between these two sets of results. This procedure appears to be a good, general, preparative method since the yields of olefins although falling off with higher olefins, does not drop below 70% even in the case of octene.<sup>24</sup>

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### Summary

1-C<sup>14</sup>-propene-1 has been prepared. The migration of the double bond under a variety of experimental conditions in the preparation of propene has been investigated. The mechanism of the permanganate oxidation of the labelled propene has been examined. It has been found to proceed by several paths the relative importance of which depends upon the experimental conditions, especially the *p*H.

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(21) R. H. Ewell and P. E. Hardy, *ibid.*, **63**, 3460 (1941).

(22) J. von Braun, *Ann.*, **382**, 1 (1911).

(23) W. Hanhart and C. K. Ingold, *J. Chem. Soc.*, 997 (1927).

(24) C. K. Ingold and C. C. N. Vass, *ibid.*, 3125 (1928).