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Preparation of 1-C14-Propene-1 and the Mechanism of Permanganate Oxidation of Propene

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PREPARATION OF 1-C¹⁴-PROPENE-1 AND THE
MECHANISM OF PERMANGANATE OXIDATION OF PROPENE

by

B. A. Fries and M. Calvin

10 December 1947

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ABSTRACT.

1-C¹⁴-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 pH.

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PREPARATION OF 1-C¹⁴-PROPENE-1 AND THE
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The preparation of 1-C¹⁴-propene-1 was undertaken in order to have available propene labelled in a terminal position and, incidently, to study the stability of the double bond 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 problem 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 C¹⁴ labelled materials, while others were discarded when preliminary tests with nonradioactive materials indicated either very poor yields or impure products. The first three

* Our thanks are due to Mrs. Martha Kirk for her technical assistance in this work and particularly for the performance of many of the isotopic analyses.

** While on leave from California Research Corporation, Richmond, California.

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 hydroxide
- 4) Pyrolysis of methyl n-propyl xanthate
- 5) Dehydrobromination of n-propyl bromide with alcoholic KOH

Extensive rearrangement of the double bond was found to occur when preparing propene by dehydration with metaphosphoric acid and with heated Al_2O_3 . However, the pyrolysis of the quaternary ammonium base gave little, if any, rearrangement and the product consisted principally of 1- C^{14} -propene-1 ($\text{CH}_3\text{-CH}^*\text{=CH}_2$), whereas in the other cases, mixtures of 1- C^{14} -propene-1 and 3- C^{14} -propene-1 ($\text{CH}_3\text{-CH}^*\text{=CH}_2$) were obtained.

Degradation Procedure

The important features desired in the degradative process include:

- 1) minimum number of operations
- 2) easy separation of the products of the degradation reaction
- 3) unequivocal identification of the origin of these products.

Here again several choices were available, among them, oxidative degradation with permanganate and dichromate, ozonolysis, and glycol formation with hydrogen peroxide 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.

Permanganate Oxidation of Propene.

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 (1) reported that propylene glycol was converted quantitatively to acetic acid and CO_2 with neutral permanganate at 50°C , although in the presence of alkali, oxalic acid was formed. Hence, examination of the acetic and carbonic acids for C^{14} 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 was used to agitate the aqueous phase. An amount of 0.4 N KMnO_4 , calculated to be just sufficient to oxidize propene to propylene glycol, was added over a period of 45 minutes. This was followed by the addition of 110 percent of the amount of 2N KMnO_4 required for the oxidation of propylene glycol to acetic and carbonic acids. This addition required 45 minutes, after which the solution was stirred 15 minutes more. An H_2SO_4 -acidified solution of FeSO_4 was added to reduce all manganese to the manganous state and simultaneously liberate CO_2 . The flask was connected to a NaOH absorber and swept with nitrogen gas to collect this CO_2 fraction. The solution remaining was steam distilled to recover acetic acid. This latter was titrated with NaOH and evaporated to dryness as sodium acetate. The weight of the salt obtained, 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.

1. W. L. Evans, J. Am. Chem. Soc., 45, 171 (1923).

TABLE I

Oxidation of Propene with KMnO_4 at Several Values of pH.

Starting Solution	0.04N NaOH	0.02N NaOH	0.1M PO_4^{3-} pH 7.4	distilled water	0.1M PO_4^{3-} pH 6.0	0.1M PO_4^{3-} pH 4.0
Temp. °C.	35	35	35	35	25	25
$\frac{\text{Moles CO}_2}{\text{Moles C}_3\text{H}_6}$	1.54	1.31	1.28	1.11	0.94	0.94
$\frac{\text{Moles Acetic Acid}}{\text{Moles C}_3\text{H}_6}$	0.18	0.38	0.46	0.57	0.73	0.70
$\frac{\text{Acetic Acid}}{\text{CO}_2}$	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 CO_2 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 H_2SO_4 and 0.5 M in CrO_3 , heated to boiling and swept with oxygen for one hour. Considerable carbon and C^{14} activity was found in this fraction. The inclusion of this additional carbon boosted the total carbon recovery to 85-90%.

There were several indications that this oxidizable residue was oxalic acid. First, oxalic acid may be found during alkaline permanganate oxidation of propylene glycol (1). Second, oxalic acid is oxidized very slowly at 25°C and pH 4 by KMnO_4 or MnO_2 and therefore, the oxalic acid would be stable, if present. Third, the nature of the analytical procedure eliminates the possibility of a one carbon compound, since these compounds (CH_3OH , HCHO , HCOOH), 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 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 MnO_2 by centrifugation. Inactive sodium oxalate was added as a carrier and the oxalate was ultimately precipitated as CaC_2O_4 after separation from phosphate by employing the scheme of Swift (2). 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 be carried down with the CaC_2O_4 . The CaC_2O_4 was titrated with permanganate

2. E. H. Swift, A System of Chemical Analysis, Prentice-Hall, Inc., New York, 1940, p. 469 et. seq.

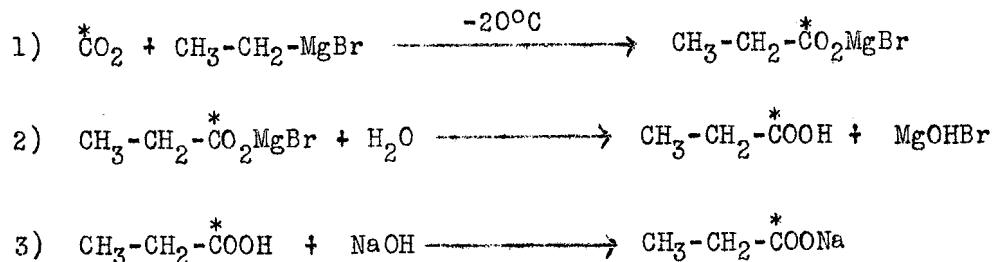
in the usual manner, and the CO_2 was collected and analyzed for C^{14} activity. The titration agreed within 3 percent with the formula CaC_2O_4 for the calcium precipitate; however, since the amount of carrier was about four times the amount of oxalate expected, the presence of other insoluble calcium salts might have been masked. The amount of C^{14} found as oxalate was about 70% of the amount found by direct CrO_3 oxidation of the residue in another experiment using the same radioactive propene.

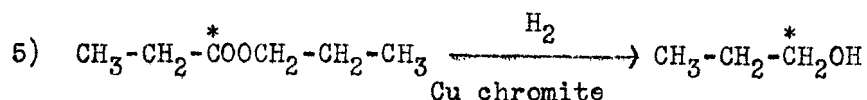
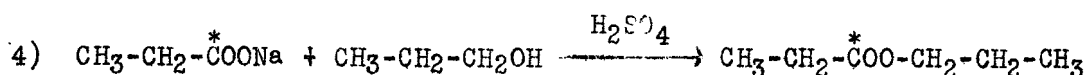
Ozonolysis Method.

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°C and 10 ml. water added and shaken with the ethyl chloride. The ethyl chloride was removed by evaporation under house vacuum. The aqueous solution, which now contains formaldehyde and acetaldehyde, was made alkaline with NaOH . Excess KMnO_4 was added and the solution heated to 50°C . The formaldehyde was oxidized to CO_2 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.

Preparation of 1- C^{14} -n-Propanol ($\text{CH}_3\text{-CH}_2\text{-CH}_2^*\text{OH}$)

The principal intermediate in the synthesis of propylene was propanol. The starting point of this synthesis was BaCO_3 containing C^{14} from which C^{14}O_2 was obtained. The following series of reactions outline the procedure by which n-propanol was prepared.





The procedure for carbonation of Grignard reagent in a vacuum system has been described (3). In the present case, the ethyl magnesium bromide was prepared under nitrogen and 25 millimoles of the reagent was transferred with a syringe into a flask connected to the vacuum line. The CO_2 was generated by the addition of concentrated H_2SO_4 to 4.12 gms. (20.9 millimoles) of BaCO_3 containing approximately 800 microcuries of Cl^{14} . The CO_2 was recovered in a trap cooled with liquid nitrogen and then allowed to distill into the Grignard reagent held at -20°C . when the absorption of carbon dioxide was complete, the solution was cooled to -80°C and the Grignard compound decomposed by the addition of dilute H_2SO_4 and warming. The ether was evaporated under house vacuum, bromide ion was precipitated by the addition of excess Ag_2SO_4 and the solution steam distilled to recover propionic acid. After titration with NaOH , the solution was evaporated to dryness and solid sodium propionate was recovered with 94.8% yield. A very high specific activity product was not required in this experiment and a large dilution of Cl^{14} 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 gms. (16.9 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°C) 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°C , the flask was cooled and 1.0 gms. of CaCO_3 was added to destroy excess H_2SO_4 . The distillation was continued, the remaining benzene being removed as the binary azeotrope (77.1°C) with n-propyl alcohol. The distillation was stopped when the temperature reached 92°C . The ester-alcohol solution remaining was removed from the $\text{CaSO}_4\text{-CaCO}_3$ residue by vacuum transfer. This solution, about 8 ml, was pipetted into a high pressure hydrogenation bomb (Aminco, 43 ml. size) containing 2.0 gms. of copper chromite catalyst (Adkins). The bomb was charged with 2500 p.s.i. of H_2 , heated to 250°C and maintained there for nine hours. The contents of the bomb were transferred on the vacuum line into a flask containing CaO 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 $96\text{-}97^\circ\text{C}$ was recovered. The fraction boiling below 96°C (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°C fractions were combined with the first fraction collected. In this manner 10.3 ml. of 1-C¹⁴-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 ethyl magnesium 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. The yields and losses of C¹⁴ in various fractions are shown in Table II. The final product contained 4.58×10^6 c/min/ml. or about 50 μ c/ml.

TABLE II

C¹⁴ Yields and Losses in Preparation of 1-C¹⁴-n-propanol

Sample	Total c/min.	%
Starting BaCO ₃	7.63×10^7	
Residue 1 Grignard residues	4.05×10^4	0.6
Sodium Propionate (94.8% yield)	7.25×10^7	95
Starting sodium propionate for esterification	5.94×10^7	
Residue 2 Azeo. dist. 67-74° fraction	0.14×10^7	2.4
Residue 3 Azeo. dist. 74-92° fraction	0.11×10^7	1.9
Residue 4 Final dist. residues	0.57×10^7	9.6
Final n-propanol	4.72×10^7	79.5
C ¹⁴ material balance		93.4

Preparation of 1-C¹⁴-n-propyl bromide.- The propyl bromide was prepared from n-propanol by the phosphorus and bromine method (4), but additional phosphorus and Br₂ were added. The yield of propyl bromide was 76% based on propanol. A low C¹⁴ activity sample of propanol was prepared by dilution of the high activity material for use in this preparation.

4. A. H. Blatt, Organic Syntheses. Collective Vol. I, John Wiley and Sons, Inc., New York, 1941, p. 37.

Dehydration of n-propanol with Metaphosphoric Acid. A 2 ml. sample of propanol containing 6350 c/m C^{14} 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°C according to the method of Newth (5). Water and alcohol were condensed in a trap at -20°C 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 (*). 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 Al_2O_3 . A 2 ml. portion of the above dilute propanol was dehydrated by dropwise addition over a period of 30 minutes into a vertically mounted quartz furnace tube containing Al_2O_3 at 390°C. The Al_2O_3 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 times was approximately 5 seconds. A second sample of alcohol was dehydrated over laboratory prepared Al_2O_3 obtained by precipitation of $Al(OH)_3$ from reagent grade $Al(NO_3)_3$. The catalyst temperature was 415°C 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 quarternary 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 Ag_2O was added to convert the bromide to hydroxide. After filtering $AgBr$ and excess Ag_2O the aqueous solution was boiled to dryness in a system containing a cold water condenser, a 1 N HCl wash bottle to remove $(CH_3)_3N$, a tube of Drierite and a liquid N_2 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 (6) 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 24 hours, only half the ester was decomposed. The system was swept with a slow current of nitrogen and the gases were passed through a 1 N NaOH wash bottle to remove COS and CH_3SH , then through a drying tube and finally into a liquid N_2 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.

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

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

6. I. Schurmann and C. E. Boord, J. Am. Chem. Soc. 55, 4930 (1933).

Dehydrobromination of n-propyl bromide with alcoholic KOH. Propene was prepared by refluxing the bromide with excess KOH 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 (7) reported a yield of 20% propene. Analysis of the gas sample showed 75% propene, 16% butenes, 3% i-butane, 3% ethyl propyl ether and traces of ethane, propane and propyl bromide. The use of this method was not attempted with radioactive propyl bromide.

Results and Discussion

In Table III 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 will be necessary to examine the data in this table 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 equilibrium did not occur during the analysis. Inspection of experiments 1, 2, and 3 shows 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-C¹⁴-propene-1 and 3-C¹⁴-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-C¹⁴-propene-1.

The mechanism which has been assumed for the oxidative splitting of olefins with permanganate consists of rupture of the molecule at the double bond with the production of acetic and carbonic acids in the case of propene. If the acetic acid is to be used as a measure of labelling of the methyl group of propene, it is necessary to demonstrate that all the C¹⁴ activity is present

7. J. U. Nef, Annalen, **309**, 126 (1899).

Table III
Acid Permanganate Analyses of Propene Samples

Preparative Procedure	Expt. 1 Dehydration with Metaphosphoric Acid			Expt. 2 Dehydration with Alorco Al ₂ O ₃			Expt. 3 Dehydration with Laboratory prepared Al ₂ O ₃			Expt. 4 Pyrolysis of n-propyl trimethyl ammonium hydroxide		
	Specific Activity of C ¹⁴ in starting material (c/m/millimole)	6350			6350			6350			8300	
Fraction Analyzed	CO ₂	Acetic Acid	Oxalic Acid	CO ₂	Acetic Acid	Oxalic Acid	CO ₂	Acetic Acid	Oxalic Acid	CO ₂	Acetic Acid	Oxalic Acid
Specific Activity of C ¹⁴ in Fraction (c/m/millimole C)	2790	1610	1560	3980	1100	2130	2840	1530	2020	7600	130	3810
% of total C ¹⁴ recovered in Fraction *	41	42	5.0	59	24	5.9	38	39	6.2	91	2.2	5.7
Moles/mole C ₃ H ₆	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 ¹⁴ Recovery	88			89			83			99		
Total C Recovery	94			84			89			85		

* In this calculation only the olefin content of the gas sample used in the KMnO₄ 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 C¹⁴ labelled atoms per molecule nor the isomers were known.

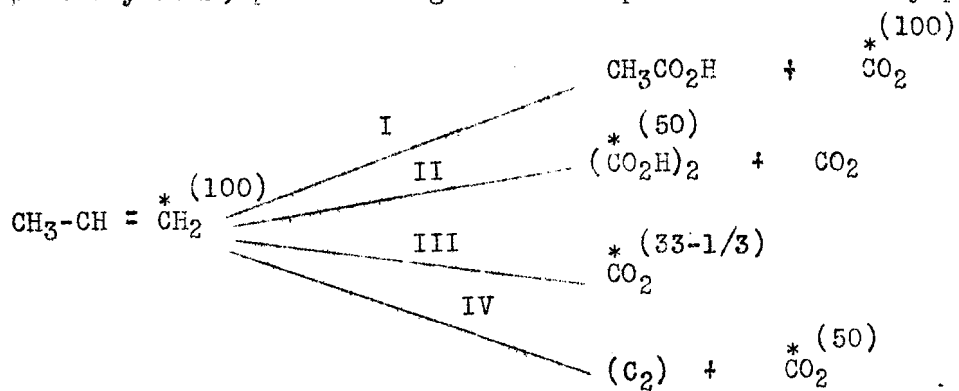
in the methyl group of the acetic acid. Therefore, on pyrolysis of a sample of barium acetate to acetone and BaCO_3 , the latter should contain no C^{14} . A sample of acetate from experiment 2, when pyrolyzed showed that 5% of the C^{14} present was present in the carboxyl group. The pyrolysis of a sample of synthetic methyl-labelled acetate (8) yielded $1\frac{1}{2}$ -2% of the total activity in the BaCO_3 which would correspond to 3-4% of the activity apparently being in the carboxyl group. Hence, the above result may be taken to mean that little, if any, carboxyl activity is present and that the carboxyl group of the acetate is derived from the central carbon atom of the propene. Therefore, in every case shown in Table III, 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 a case in which there is no activity in the acetate fraction would prove that all the labelling was at one end of the propene. This is the case in experiment 4 where only 3% of the C^{14} activity was present in the acetate. This particular propene sample was checked by the ozonozation 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^{14} -propene-1 to the extent of 97-100%, and acetic acid can arise only from the $\text{CH}_3\text{-CH}=\text{}$ portion of the molecule. Accordingly, acetate is the most reliable indicator of the activity of the CH_3 - position in propene and this is true even though acetic acid is not recovered in 100% yield.

The specific activity of the CO_2 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^{14} is located in the 1-position in the propanol,

the specific activity of this particular carbon atom is also 6350 c/m per millimole of carbon. The specific activity of the methylene carbon of the propene is therefore $6350 - (2 \times 160) = 3130$ c/m per millimole C, but the specific activity found in the CO_2 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 indicate that the CO_2 carbon is not exclusively derived from the methylene carbon, but probably from the methyl and central carbon atoms as well.

Examination of the oxalic acid fraction revealed that the oxalate contains 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. 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 III. 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 corresponds closely to that known to be present in the methylene carbon. These results demonstrate that some propene is split at the $\text{CH}_3\text{-CH}$ bond, perhaps to the extent of 15-20%. The -CH = CH_2 group is oxidized to oxalic acid, while the $\text{CH}_3\text{-}$ group is split off as a one carbon compound, presumably oxidized to CO_2 , although some may not be oxidized beyond methanol or formaldehyde. The specific activity of C^{14} in the CO_2 fraction (representing the = CH_2 group) is therefore low due to the CO_2 which arises from the methyl group and probably from the central carbon atom as well. In the alkaline oxidation of propylene glycol (1), the yield of CO_2 is over one mole per mole of glycol, while

the acetate is lower and oxalate is higher than that obtained from the acid oxidation. This led to the performance of an alkaline oxidation on the propene from experiment 4. The oxidation was carried out in the same manner as those previously described except the medium was .04 N in NaOH. The number of moles of CO₂, 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 CO₂ is very high and its specific activity is very low, indicating that a considerable portion of it has come from carbon atoms other than the methylene group of the propene. Quantitative estimates, based upon relative yields and specific activities, indicate that nearly half of the propene has been completely oxidized to carbon dioxide, the remainder going partly (1/3) to acetic acid and CO₂ and partly (1/6) to oxalic acid and CO₂. Still another route of oxidation is required to account for the small amount of activity found in the acetate fraction. This can be accounted for by some symmetrical intermediate (retaining the methyl group) such as isopropyl alcohol or acetone. We thus have three, and probably four, paths through which propene is oxidized by permanganate.



The number in parenthesis indicates the percentage of the original specific activity to be found in the atom or compound so labelled.

In the acid oxidation path I predominates (5/6) with paths II and III contributing minor and approximately equal parts. Somewhat similar conclusions were deduced for the alkaline permanganate oxidation of propionic acid by Mahinsky and Ruben (9).

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 Al_2O_3 was a 65% 1- C^{14} -propene-1 and 35% 3- C^{14} -propene-1 mixture, the propene prepared from the laboratory Al_2O_3 was approximately a 50-50 equilibrium mixture; while the propene derived from the quaternary ammonium hydroxide was a 97% 1- C^{14} -propene-1 and 3% 3- C^{14} -propene-1 mixture.

Isomerization during olefin preparation by dehydrative reactions is well known. Asinger (10) found double bond isomerization all along the carbon chain when dehydrating dodecanol with Al_2O_3 . With pure Al_2O_3 , the principal isomers were dodecene-1 and 2; however, when acidic impurities were present, more or less, equimolar quantities of all the isomers were found. Isomerization was found at temperatures as low as 250°C , even though the dehydration reaction was incomplete at this temperature. The mechanism proposed was based upon readdition, followed by splitting off, of water. Acidic impurities apparently accelerate the readdition of water. Matignon et. al. (11) obtained 15% butene-2 when dehydrating n-butanol with pure Al_2O_3 and 90% butene-2 when using impure Al_2O_3 . The isomers were determined by bromination and fractionating of the dibromides. Pines (12) obtained 100% butene-1 with pure Al_2O_3 and 99.6%

9. P. Mahinsky and S. Ruben, J. Am. Chem. Soc.

10. F. Asinger, Ber., 75B, 1247 (1942).

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

12. H. Pines, J. Am. Chem. Soc. 55, 3892 (1933).

butene-1 with commercial Al_2O_3 in the dehydration of n-butanol. His products were analyzed by low temperature distillation. Pines believes the results of Matignon et. al. disagree with his own because isomerization of the dibromides occurred during their distillation. In the present study isomerization of propene during dehydrative preparation over Al_2O_3 appeared to occur quite readily. This ease of isomerization may be due to the symmetrical structure of propene.

The preparation of olefins by dehydration of alcohols with metaphosphoric acid also gave rise to general isomerization of the double bond along the chain in the case of dodecene (10). Morgan and Hickinbottom (13) obtained only butene-2 from n-butanol. In the experiments reported here complete equilibration of propene isomers was found.

Pyrolysis of n-propyltrimethylammonium hydroxide gave essentially pure 1-C¹⁴-propene-1 in 90% yield. A side reaction of this pyrolysis results in the formation of methanol and a mixed tertiary amine. von Braun (14) found 5-10% methanol while Hanhart and Ingold (15) and Ingold and Vass (16) 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 (16).

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13. G. T. Morgan and W. J. Hickinbottom, J. Chem. Soc., Trans., 73, 97 (1923).
 14. J. von Braun, Ann., 361, 1 (1911).
 15. W. Hanhart and C. K. Ingold, J. Chem. Soc., 997 (1927).
 16. C. K. Ingold and C. C. N. Vass, J. Chem. Soc., 3125 (1928).

Summary.

1-C¹⁴-1propene-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 pH.

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