

# Carbon-14 Tracer Study of the High Temperature Oxidation of Propylene

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The mechanism for the high temperature partial oxidation of olefinic hydrocarbons is incompletely understood. This is due, in part, to the great complexity of products formed which include hydrocarbons, aldehydes, ketones, epoxides, and acids. This paper presents the results of a tracer study which was made on the mechanism of the oxidation of propylene. By the use of both propylene-3-C<sup>14</sup> and propylene-1-C<sup>14</sup> it was possible to obtain new information concerning the methods by which the various oxidation products are formed. The three-carbon-atom compounds, propylene oxide, propionaldehyde, and acrolein, were found to have retained the carbon skeleton of propylene. Evidence was obtained which supports the conclusion that allyl is formed by the recombination of two allyl radicals. Ethylene is apparently formed via an intermediate which involves allyl radical since its specific activity is independent of the position of the C<sup>14</sup> in the propylene tracer. The mechanisms responsible for methane formation are several in number, and it was not possible to determine the relative importance of each from the data obtained. The carbon monoxide and carbon dioxide mechanisms are also complex. However, the data indicate that carbon dioxide is not formed primarily by the oxidation of carbon monoxide. Plausible reaction mechanisms are suggested for most of the oxidation products which are consistent with the experimental radioactivity data.

## Introduction

During the mild oxidation of aliphatic hydrocarbons, a variety of products are formed which include olefins, aldehydes, ketones, epoxides, and acids. This complexity of products makes detailed analysis of the mechanism of the reaction extremely difficult. The present paper reports the results of a study of the oxidation of propylene in which a tracer technique has been used to help establish the course of formation of several important products.

The oxidation of propylene has been studied in both the low and high temperature regions by Shtern and Polyak,<sup>2</sup> who proposed a radical-chain scheme for the mechanism. Burgoyne and Cox<sup>3</sup> studied the high temperature oxidation with air in a flow system. They observed surface effects which are known to be characteristic of most hydrocarbon oxidation reactions. The low temperature reaction (approximately 300°) has been studied extensively by Mulcahy and Ridge.<sup>4,5</sup> They were particularly concerned with the long induction periods which are usually observed at low tempera-

tures. The most recent study of the low temperature reaction in a static system was made by Mullen and Skirrow.<sup>6</sup> They explained practically all of the main features of the reaction by the formation of the unreactive allyl radical.

The only carbon-14 tracer work that appears to have been done on propylene is that of Neimann, Lukovnikov, and co-workers,<sup>7,8</sup> in which particular attention was devoted to the problems of the mechanism of carbon oxide formation and the mechanism of acetaldehyde decomposition.

In all of the studies that have been mentioned, the reaction was followed mainly by pressure-time data which, in some cases, were supplemented by partial product analyses in which total aldehyde, total acid, etc., were determined. At the time most of the work was done it simply was not possible, with conventional chemical methods, to obtain complete product analyses. However, the technique of gas chromatography, which is now a common and very useful analytical method, allows complete product analyses to be made on a routine basis. This paper describes the results of a carbon-14 tracer study of the oxidation of propylene in which this technique was used. In addition, gas chromatography on a preparative scale was used for the separation of the total product into individual components for carbon-14 assay.

## Experimental

**Materials.** Propylene-3-C<sup>14</sup> (C<sup>14</sup>H<sub>5</sub>CH=CH<sub>2</sub>) and propylene-1-C<sup>14</sup> (CH<sub>3</sub>CH=C<sup>14</sup>H<sub>2</sub>) of 1.0 mc./mm. specific activity were supplied by Research Specialties Co., Inc., Richmond, Calif. Both compounds were purified by means of preparative gas chromatography. Research grade Phillips propylene was used without further purification to dilute the radioactive propylenes. Small amounts of ethane and propane were the impurities present in the ordinary propylene. Linde oxygen of 99% purity was used as the oxidant.

**Reactor.** The oxidation experiments were carried out in a flow-type, annular quartz reactor which was mounted in a bed of fluidized sand. The reactor consisted of the annular space between two concentric tubes of the following dimensions: inner tube, 6-mm. i.d. × 9-mm. o.d. × 64 mm.; outer tube, 12-mm. i.d. × 15-mm. o.d. × 64 mm. The temperature of the reactor was maintained constant to ±3° over a 50-cm. length. The effective volume of the reactor was calculated for each experiment from the measured temperature gradient and was usually of the order of

(1) Nuclear Science and Engineering Corp., Pittsburgh, Pa. 15236.  
(2) (a) V. Ya. Shtern and S. S. Polyak, *Zh. Fiz. Khim.*, **27**, 950 (1953);  
(b) *Dokl. Akad. Nauk SSSR*, **95**, 1231 (1954).  
(3) J. H. Burgoyne and R. A. Cox, *J. Chem. Soc.*, 876 (1953).  
(4) M. F. R. Mulcahy and M. J. Ridge, *Trans. Faraday Soc.*, **49**, 906 (1953).  
(5) M. F. R. Mulcahy and M. J. Ridge, *ibid.*, **49**, 1297 (1953).

(6) J. D. Mullen and G. Skirrow, *Proc. Roy. Soc. (London)*, **A244**, 312 (1958).  
(7) A. F. Lukovnikov and M. B. Neimann, *Dokl. Akad. Nauk SSSR*, **91**, 581 (1953).  
(8) M. B. Neimann, V. Ya. Efremov, N. K. Serdyuk, and A. F. Lukovnikov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 408 (1956).

Table I. Yields, Specific Activities, and Relative Activities of Propylene-3-C<sup>14</sup> Oxidation Products<sup>a</sup>

Product	Moles/100 moles of reactant	Sp. act., amp./cc. × 10 <sup>14</sup>	Relative activity	Interpretation
Methane	1.003	2.69	0.79	Approx. 81% from carbon 3
Carbon monoxide	4.644	0.477	0.14	Approx. 85% from carbons 1 and 2
Carbon dioxide	1.574	1.09	0.32	Approx. 33% from carbon 3
Ethylene	1.601	1.88	0.55	Approx. 50% from carbons 2 and 3
Propylene-3-C <sup>14</sup>	60.66	3.26	0.953	
Propylene-2-C <sup>14</sup>		0.068	0.02	
Propylene-1-C <sup>14</sup>		0.082	0.027	
Acetaldehyde	0.844	3.03	0.89	Approx. 93% from carbons 2 and 3
Propylene oxide	0.236	3.68	1.08	Contain carbon skeleton of propylene
Propionaldehyde	0.414	3.68	1.08	
Acrolein	0.781	3.14	0.92	
Acetone	0.109	6.61	1.94	Formed by combination of 2 or more small fragments
Biallyl	0.845	7.45	2.18	Formed by combination of 2 allyl radicals

<sup>a</sup> Propylene/oxygen = 2.41; pressure 1 atm.; temperature 625°; propylene conversion = 13.2%; oxygen conversion = 35.3%; residence time 1.03 sec.; propylene isotopic composition: 95.7% C<sup>14</sup>H<sub>3</sub>CH=CH<sub>2</sub>, 2.0% CH<sub>3</sub>C<sup>14</sup>H=CH<sub>2</sub>, 2.3% CH<sub>3</sub>CH=C<sup>14</sup>H<sub>2</sub>.

31 cc. Temperatures were measured with a platinum-13% rhodium thermocouple which was situated in the inner tube of the reactor.

The radioactive propylene used in the experiments was diluted by approximately a factor of 4000 with ordinary Phillips research grade propylene. The resulting mixture was stored in a small gas cylinder under approximately 6 atm. pressure. The propylene and oxygen were fed separately but were premixed before entering the reactor. Product samples were collected by drawing off a portion of the exit gas stream into evacuated sample flasks. These samples were taken at reduced pressure (200-400 mm.) in order to prevent the condensation of the normally liquid organic oxygenated products.

**Methods of Analysis.** Most of the product analyses were performed with a Perkin-Elmer Model 154-B vapor fractometer. Three columns were necessary in order to obtain complete analyses. A Linde 5A Molecular Sieve column was used for oxygen, carbon monoxide, and methane. Carbon dioxide, ethylene, and propylene were determined with a silica gel column. Biallyl and the oxygenated organic compounds were determined on a column packed with 20% by weight of β,β'-oxydipropionitrile on Chromosorb. Mass spectrometry was used in cases of doubt concerning the identification of compounds separated by gas chromatography.

**Method for Separation and Collection of Products.** In order to obtain radioactivity data on the products of oxidation, it is necessary to separate and collect the individual components of the total product. This was accomplished by preparative gas chromatography. In this technique relatively large volumes of product gas (~100 cc. NTP) were separated with the same three columns mentioned. However, in order to obtain more efficient separation of the large samples, the columns were thermostated at lower than usual temperatures. As the separated components were eluted from the chromatographic column, they were collected into individual traps cooled to -195°. In order to collect methane and carbon monoxide it was necessary to pack the cooled traps with activated charcoal.

**Determination of Distribution of Carbon-14 in Propylene.** The distribution of carbon-14 among the three carbon atoms of both propylene isotopes was

determined by a selective oxidation method modified slightly from one described by Fries and Calvin.<sup>9</sup> In the case of propylene-3-C<sup>14</sup> there were approximately 2% of CH<sub>3</sub>C<sup>14</sup>H=CH<sub>2</sub> and 2.3% of CH<sub>3</sub>-CH=C<sup>14</sup>H<sub>2</sub> present as impurities. The propylene-1-C<sup>14</sup> was demonstrated to be essentially pure.

**Radioassay of Oxidation Products.** The method used for the determination of the specific activities of the products of the reaction has been described previously<sup>10</sup> and will not be repeated here in detail. All that is involved is the transfer of the separated components into an ionization chamber where they are counted with an Applied Physics Corp. Model 30 vibrating-reed electrometer. Then an analysis by gas chromatography of an aliquot of the radioactive material contained in the ionization chamber determines the amount of radioactive material present. The specific activity is obtained by dividing the ionization current by the volume of radioactive material contained in the ionization chamber.

## Results

Table I contains the data which were obtained on propylene-3-C<sup>14</sup> oxidation at 625°, 1 atm., 1.03-sec. residence time, and a propylene-to-oxygen ratio of 2.41. Under this particular set of experimental conditions 13.2% of the propylene and 35.3% of the oxygen reacted to give the products shown, as well as some other products which are not listed. The only products given in the table are those for which radioactivity data were obtained.

In Table I the number of moles of each product/100 moles of total reactant is given in column 2. Since approximately 100 cc. of total product was separated into individual components, the numbers in this column represent closely the number of cc. (STP) of each component that was counted. The specific activities in ion current/cc. (STP) of vapor are given in column 3. The relative activity values, defined as the specific activity relative to propylene, are given in column 4. Finally, it is possible to interpret the relative activity data in terms of the origin of products. These interpretations are given in column 5.

(9) B. A. Fries and M. Calvin, *J. Am. Chem. Soc.*, 70, 2235 (1948).

(10) E. R. White and H. G. Davis, *Anal. Chem.*, in press.

**Table II.** Yields, Specific Activities, and Relative Activities of Propylene-1-C<sup>14</sup> Oxidation Products<sup>a</sup>

Product	Moles/100 moles of reactant	Sp. act., amp./cc. × 10 <sup>14</sup>	Relative activity	Interpretation
Methane	0.70	0.54	0.09	9% from carbon 1
Carbon monoxide	3.22	2.10	0.35	Approx. 33% from carbon 1
Ethylene	1.11	3.36	0.56	Approx. 50% from carbons 1 and 2
Propylene-1-C <sup>14</sup>	58.9	6.00	1.00	
Acetaldehyde	0.59	2.10	0.35	Approx. 33% from carbons 1 and 2
Propylene oxide	0.16	5.88	0.98	Contain carbon skeleton of propylene
Propionaldehyde	0.29	5.40	0.90	
Acrolein	0.54	6.55	1.09	
Biallyl	0.48	13.75	2.29	Formed by combination of 2 allyl radicals

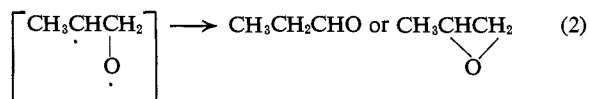
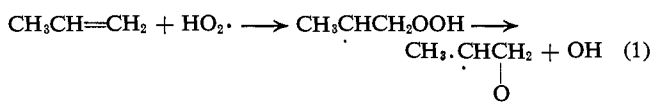
<sup>a</sup> Propylene/oxygen = 1.90; pressure 1 atm.; temperature 639°; propylene conversion = 10.1%; oxygen conversion = 27.0%; residence time 0.85 sec.; propylene isotopic composition: 100% CH<sub>3</sub>CH=C<sup>14</sup>H<sub>2</sub>.

Table II is similar in every detail to Table I, except that the results of the oxidation of propylene-1-C<sup>14</sup> under similar conditions are presented.

### Discussion

In this section, plausible mechanisms for the formation of the various oxidation products are suggested in light of the relative activity data given in Tables I and II. In some cases the interpretation of this data is obvious, but, generally, detailed explanations are required. It is to be emphasized, however, that the mechanisms which are given are not unique but are only the ones which seem to be the most consistent with the experimental data.

*Propylene Oxide and Propionaldehyde.* As is indicated in both Tables I and II, these two products contain the carbon skeleton of propylene since the relative activities are, within experimental error, equal to unity. A similar result was obtained by Yokley and Ferguson<sup>11</sup> in their investigation of the oxidation of CH<sub>3</sub>C<sup>13</sup>H<sub>2</sub>CH<sub>3</sub>. A plausible scheme which explains both of these results involves the direct interaction of propylene with the HO<sub>2</sub>· radical as indicated



These over-all reactions have been postulated by Falconer and Knox<sup>12</sup> to explain the enhanced yields when propylene is added to a mixture of propane and oxygen.

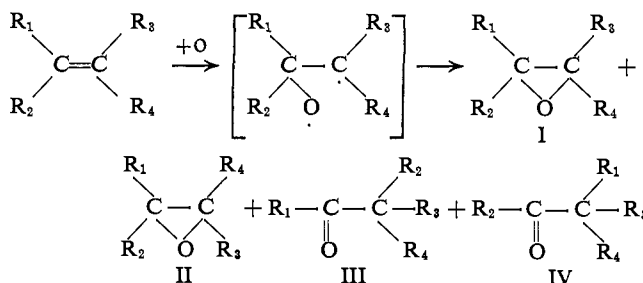
A somewhat similar mechanism was proposed by Cvetanovic<sup>13</sup> to explain the formation of propylene oxide and propionaldehyde in the nitrous oxide photo-oxidation of propylene. In his scheme the intermediate CH<sub>3</sub>CHC(O)H<sub>2</sub> is formed by the addition of an oxygen atom to the less substituted carbon, namely the methylene carbon. Then, in the same manner as indicated in (2), propylene oxide and propionaldehyde are formed from the triplet biradical by simple stabilization and hydrogen atom migration, respectively.

(11) C. R. Yokley and R. E. Ferguson, "Seventh Symposium on Combustion," Butterworths Publications, London, 1959, p. 113.

(12) W. E. Falconer and J. H. Knox, *Proc. Roy. Soc. (London)*, **A250**, 493 (1959).

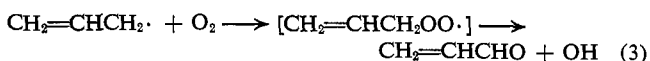
(13) R. J. Cvetanovic, *Can. J. Chem.*, **36**, 623 (1958).

It should, perhaps, be mentioned that the mechanism which has been proposed for the case of propylene should be applicable to all olefinic compounds. Cvetanovic investigated the series propylene, butene-1, isobutene, *cis*-butene-2, *trans*-butene-3, *cis*-pentene-2, and tetramethylethylene and found that his experimental findings could be explained by assuming that the oxygen atoms add to one of the carbon atoms of the olefinic double bond to form a short-lived biradical which rapidly rearranges into isomeric epoxy and carbonyl compounds. In the case of unsymmetrical olefins, the addition is to the less substituted carbon atom. The rearrangements involve migration of radicals or hydrogen atoms from the carbon atom to which oxygen is attached to the other carbon atom of the original double bond. The scheme for the reaction of oxygen atoms with a generalized olefin is

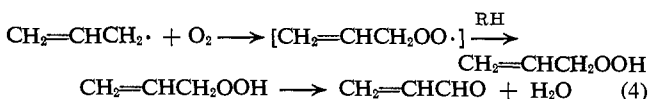


In this scheme R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, and R<sub>4</sub> are alkyl radicals or hydrogen atoms, and the first carbon atom of the double bond is assumed to be "less substituted." Each of the compounds represented by I to IV was produced in substantial quantities with each of the olefins studied.

*Acrolein.* This compound also contains the carbon skeleton of propylene since the relative activities given in Tables I and II are nearly equal to unity. A mechanism which explains this result satisfactorily involves the reaction of allyl radical with oxygen



A reaction similar to this one was proposed by Mullen and Skirrow.<sup>6</sup> Since their studies were conducted at low temperatures (340–440°), they assumed the reaction to proceed through a hydroperoxide.

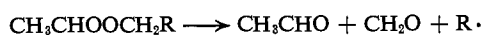
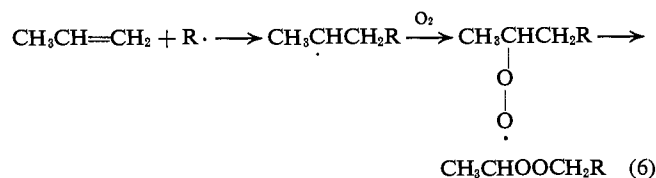


However, at the high temperature involved in this investigation, it is extremely doubtful if the hydroperoxide would form. Thus, eq. 3 is favored over eq. 4.

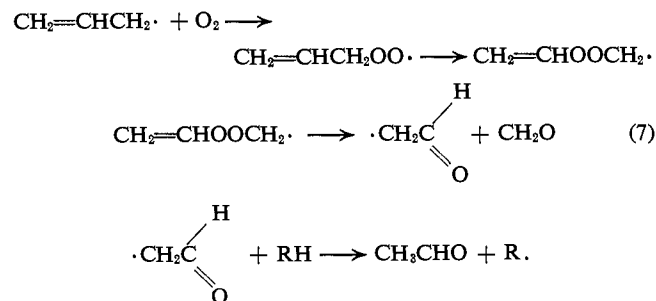
*Acetaldehyde.* The relative activity data for this compound are not easy to interpret. If it is assumed that acetaldehyde is an intact, two-carbon-atom fragment of propylene, then it can be formed either from carbons 2 and 3 or from carbons 1 and 2. The values given in Tables I and II indicate that both types are formed, with the (2, 3) compound favored. However, in either case there should be no activity in the carbonyl carbon atom since this atom is derived from the middle carbon atom of propylene. If, on the other hand, some of the acetaldehyde is formed by reactions which do not require it to be an intact, two-carbon-atom fragment of propylene, it is possible for the carbonyl atom to be radioactive. In order to determine the fraction of the total activity contained in the carbonyl carbon, samples of acetaldehyde were isolated from the product sample of each run and were degraded to methane and carbon monoxide by heating the samples in sealed quartz tubes. In each case, radioactivity assays on the methane and carbon monoxide indicated that about 18% of the total activity of the acetaldehydes was contained in the carbonyl carbon. This result requires an explanation for the formation of acetaldehyde by some mechanism which introduces activity into the carbonyl carbon. One likely possibility is the recombination of methyl and formyl radicals.



In this reaction the formyl radical is probably derived from formaldehyde. No radioactivity assays were performed for formaldehyde because it was not possible to isolate it by gas chromatography. However, it is highly unlikely that formaldehyde is unradioactive since it is probably formed by several different reactions. The mechanism which is proposed to explain the formation of the (3, 2) acetaldehyde is



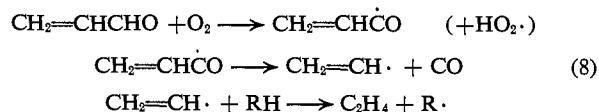
A very similar sequence of reactions was proposed by Mullen and Skirrow.<sup>6</sup> A possible method of (1, 2) acetaldehyde formation is through the reaction



Of course, (7) leads also to the formation of (3, 2) acetaldehyde 50% of the time since the allyl radical

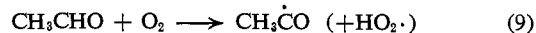
precursor with its two resonance forms effectively allows an interchange of activity to occur between carbons 1 and 3. Reaction 7 has been postulated by Shtern and Polyak<sup>14</sup> in the oxidation of propylene at 370°. Internal rearrangements similar to those that occur in reactions 6 and 7 have been proposed by Semenov<sup>15</sup> in hydrocarbon oxidation reactions.

*Ethylene.* As is evident from Tables I and II, the relative activity of ethylene is approximately half that of propylene regardless of whether propylene-3-C<sup>14</sup> or propylene-1-C<sup>14</sup> is used. This fact strongly suggests that ethylene is produced by some mechanism which involves the allyl radical as a precursor. A mechanism which satisfies this requirement is the decomposition (oxidation) of acrolein



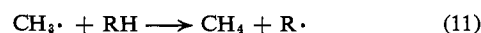
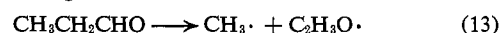
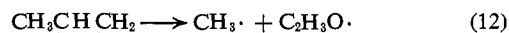
Presumably, the carbon-14 is distributed equally between the two end carbons of acrolein because the allyl radical is the precursor. Therefore, ethylene formed by this mechanism would have a relative activity of 0.5 regardless of whether propylene-3-C<sup>14</sup> or propylene-1-C<sup>14</sup> was used as the tracer.

*Methane.* A likely precursor of methane is acetaldehyde, and the following sequence of reactions is frequently postulated to explain its formation.



If acetaldehyde is, indeed, formed by this mechanism, then the relative activity of methane should be approximately equal to the relative activity of the methyl group of acetaldehyde. As previously mentioned, 82% of the carbon-14 of acetaldehyde is contained in the methyl carbon. Thus, the relative activity of the methyl group is  $0.89 \times 0.82 = 0.73$  when propylene-3-C<sup>14</sup> is the tracer (see Table I). This value is close enough to 0.79, the value for methane, to suggest that acetaldehyde is, in fact, a precursor of methane.

However, if the relative activities of methane and the methyl group of acetaldehyde of Table II are compared, it is clear that methane must also be formed by one or more additional mechanisms. In this case the value for methane of 0.09 is much less than the value for the methyl group of acetaldehyde ( $0.82 \times 0.35 = 0.287$ ). The fraction of methane formed from acetaldehyde is approximately  $0.09/0.287 = 0.31$ . Thus, 69% of the methane is formed by mechanisms which do not involve acetaldehyde as a precursor. Two likely possibilities are the decomposition of propylene oxide and propionaldehyde followed by hydrogen abstraction by methyl radical.



(14) V. Ya. Shtern and S. S. Polyak, *Dokl. Akad. Nauk SSSR*, **85**, 161 (1952).

(15) N. N. Semenov, "Some Problems of Chemical Kinetics and Reactivity," Vol. 1, Pergamon Press, Inc., New York, N. Y., 1958, p. 104.

Since it has been demonstrated that propylene oxide and propionaldehyde are formed directly from propylene, it follows that, when the propylene-1-C<sup>14</sup> is used, (12) and (13) lead to the production of non-radioactive methane while methane with a relative activity of approximately 0.95 is produced when propylene-3-C<sup>14</sup> is used.

If methane is formed according to eq. 9-13, as indicated, it should be possible to calculate its relative activity when propylene-3-C<sup>14</sup> is used. When this is done, a value of 0.88 is obtained. The experimental value given in Table I is 0.79. In view of the complexity of the system and the fact that some reactions may have been neglected, the agreement seems satisfactory.

*Carbon Monoxide.* The relative activity values given in Tables I and II indicate that about 50% of the carbon monoxide is formed from the middle carbon and 50% from the two end carbons. Some of the probable reactions which can account for the CO formation are (8) and (10) and



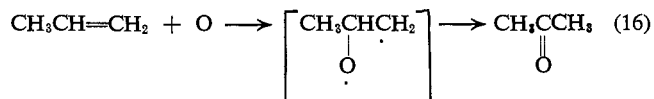
Reaction 10 is postulated frequently<sup>2,15</sup> in hydrocarbon oxidation mechanisms and is frequently encountered in photochemistry. Likewise, the thermal instability of the HCO· radical is well recognized, and reaction 15 has been frequently postulated and discussed. Reactions 8 and 14 are similar to 10 and 15 and should occur readily in the present system.

*Carbon Dioxide.* A relative activity of 0.32 in Table I indicates that approximately one-third of the carbon dioxide is formed from the methyl group of propylene. This result suggests a random formation from all three carbon atoms of propylene. Unfortunately, no data were obtained for this product when propylene-1-C<sup>14</sup> was used as the tracer so that this point was not verified. However, it is likely that carbon dioxide is formed in many different ways, and it is highly unlikely that any one carbon atom is preferred.

One process that is mentioned frequently to explain the formation of carbon dioxide is the oxidation of carbon monoxide. In order for this process to be important, the relative activity of carbon monoxide should be at least as great as that of carbon dioxide. An inspection of Table I shows that the relative activity of carbon monoxide is less than half that of carbon dioxide. It is only possible to conclude from this that

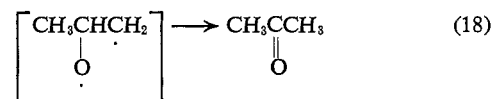
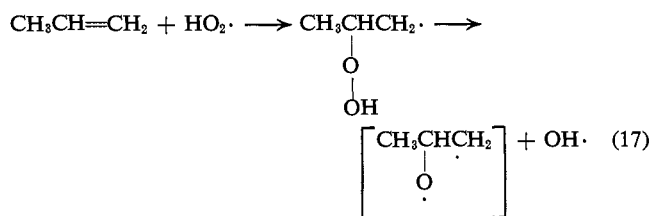
oxidation of carbon monoxide is not the sole or even principal method by which carbon dioxide is formed. A similar result was obtained by Neimann<sup>8</sup> and his co-workers in their investigation of the oxidation of propylene in the presence of C<sup>14</sup>O.

*Acetone.* A minor product of the nitrous oxide photooxidation of propylene is acetone. Cvetanović<sup>13</sup> proposed that small amounts of this compound could be formed by oxygen atom addition to the "more substituted" carbon atom of the double bond according to

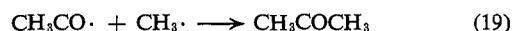


It is seen from this reaction that acetone is formed directly from propylene when the intermediate biradical rearranges to a stable form by hydrogen atom migration.

In the thermal oxidation by molecular oxygen it is conceivable that acetone could be formed directly from propylene by a similar mechanism



Obviously, this mechanism requires that the relative activity of acetone be unity since the carbon skeleton of propylene is retained. Owing to an unfortunate accident in which the acetone fraction was lost, no data are given for this product in Table II. However, the value of 1.94 for the relative activity given in Table I indicates that this product is not formed directly from propylene. Instead, it must be formed from the combination of two or more radioactive fragments. One possibility is the reaction



in which the acetyl radical is formed from acetaldehyde or else from the combination of the methyl radical with carbon monoxide. Evidence was obtained for (19) by Yokley and Ferguson<sup>11</sup> in their work on the oxidation of CH<sub>3</sub>C<sup>18</sup>H<sub>2</sub>CH<sub>3</sub>.