JOURNAL OF CATALYSIS 2, 58–62 (1963)

Mechanism of Propylene Oxidation over Cuprous Oxide

H. H. VOGE, C. D. WAGNER, AND D. P. STEVENSON

From the Shell Development Company, Emeryville, California

Received December 4, 1962

Propylene containing C^{13} in the methyl group was oxidized with oxygen to acrolein over a cuprous oxide catalyst at 300°C. Half the heavy carbon in the acrolein product was found in the carbonyl group. Isomerization of unreacted propylene was incomplete, proceeding 38% of the way to equilibrium. The distribution of C^{13} in the acrolein indicates initial removal of a hydrogen atom from the methyl group to form an allyl intermediate that is rapidly isomerized by exchange of ends prior to addition of an oxygen atom. Carbon dioxide comes largely from complete oxidation of the acrolein.

INTRODUCTION

The oxidation of propylene to acrolein by reaction with molecular oxygen over cuprous oxide was discovered some time ago (*1*). The mechanism of this important reaction conceivably involves several alternatives, including initial removal of a hydrogen atom from the methyl group, or addition of an oxygen atom to the double bond. Marking one end of the propylene molecule to permit determination of which end becomes converted to a carbonyl group offers a possible method of investigation. Therefore $CH_2{=}CH{-}C^{13}H_3$ was prepared and oxidized to acrolein over a cuprous oxide catalyst. The amount of C^{13} in the CHO group of the recovered acrolein was determined by using a mass spectrometer. The results, detailed below, gave evidence for initial removal of a hydrogen atom from the methyl group to form a labile allyl intermediate. Evidence for the same mechanism over a similar cuprous oxide catalyst, and also over bismuth molybdate, has been obtained by C. R. Adams and T. J. Jennings of this laboratory by another method, using propylene containing deuterium (*2*).

EXPERIMENTAL

The 1-propene-3-C^{13} was prepared from three grams of methyl-C^{13} iodide containing 50% C^{13}, obtained from Eastman Kodak Company. The iodide was first converted to the bromide by bromine and water at 0°. The bromide was then converted to the Grignard, and to propylene by the method of Swallen and Boord (*3*). The yield from the bromide was 60%; the over-all yield from the iodide was 50%. The mass spectrum of this product is discussed in the last section of this paper.

Oxidation was done in a glass reaction system in which a gaseous mixture was circulated over 10 cc of granular catalyst (*4*). The catalyst consisted of Cu_2O on 8–14 mesh Johns-Manville Celite VIII (a bonded diatomite); it was prepared by impregnating the acid- and water-washed support with cupric nitrate solution, drying, and calcining in air at 450°C. The Cu content was 14.4%. The catalyst was brought to the cuprous oxide state by flowing propylene over it at 300°C for 15 min and then flowing a mixture containing 91% propylene and 9% oxygen for one hour. The system was then evacuated and charged with the mixture for recycle operation. Here the reaction gases, after leaving the hot catalyst, passed through a trap at −78°C to collect acrolein and water. The reaction system, which had an internal volume of 680 ml, was at room temperature except for the hot catalyst and the cold trap. In the experiment under discussion the system was charged with 100.3 mm of tagged propylene and 30.7 mm of oxygen. This mixture was circulated for 9 min at a rate that gave a total of three or four passes over the catalyst. The total pressure drop was 19.5 mm, corresponding to reaction of about 70% of the oxygen and 8.8% of the propylene. Analyses showed that the selectivity of oxidation to acrolein, based on propylene reacted, was about 58%.

TABLE 1

ANALYSES OF 1-PROPENE-3-C^{13} AND PRODUCTS[a]

Component	Original propylene	Acrolein product	Bottom 40% of acrolein	Unreacted $C_3H_6 + CO_2$	CO_2 from unreacted C_3H_6[b]
C_3H_6–C_2^{13}	1.1	—	—	1.0	—
C_3H_6–C_1^{13}	51.3	2.9	—	45.1	—
C_3H_6–C_0^{13}	47.5	—	—	43.2	—
C_3H_4O–C_2^{13}	—	1.0	1.0	—	—
C_3H_4O–C_1^{13}	—	45.1[c]	48.9[d]	—	—
C_3H_4O–C_0^{13}	—	43.3	47.2	—	—
Propionaldehyde	—	1.9	2.7	—	—
Acetaldehyde	—	ca. 6	<0.1	—	—
$C^{13}O_2$	—	<0.5	<0.1	1.86	11.0
$C^{12}O_2$	—			8.85	89.0

[a] Mole percentage compositions of gaseous samples.

[b] Product obtained by permanganate oxidation of unreacted C_3H_6.

[c] For ions attributable to this species, mass 30/mass 57 = 0.20.

[d] For ions attributable to this species, mass 30/mass 57 = 0.22.

Products of the oxidation, besides acrolein, water, and carbon dioxide, include small amounts of CO, acetaldehyde, propionaldehyde, acetone, formaldehyde, and acetic acid. To recover primarily acrolein, the trap at —78° was flushed with air to remove propylene and CO_2. Then the acrolein was distilled in vacuum from the trap at —78° to another at —195°, and the distillation was stopped when the pressure indicated by a thermocouple gage fell abruptly, thus leaving water and polymer behind. One sample of acrolein was taken at this stage and another after a second distillation during which the most volatile 60% of the acrolein was discarded to reject lower boiling aldehydes.

TABLE 2

COMPUTED DATA FROM ANALYSES

Material	Group	C^{13} Content of group (%)	Percentage of total C^{13} in molecule found in group
Original C_3H_6	—CH_3	51.4	96
Original C_3H_6	=CH_2	1.1	2
Acrolein product	—CHO	26	50
Acrolein product, bottom 40%	—CHO	28	55
CO_2 product	CO_2	17.4	100
Unreacted C_3H_6	=CH_2	10.7	20

Analyses were made with a Westinghouse mass spectrometer in the usual way. The C^{13} content of the carbonyl group in the acrolein was judged from the ratio of mass 30 ions to mass 57 ions attributable to acrolein. These ions for acrolein containing C^{13} correspond to the ions of mass 29 (CHO) and 56 (C_3H_4O) from normal acrolein. In the normal acrolein spectrum, the ratio of mass 29 to mass 56 was 0.398 under the spectrometer conditions used. Thus a ratio of mass 30 to mass 57 of 0.20 meant that 50% of the C^{13} in the marked acrolein was present in the carbonyl group.

Feed propylene and recovered unreacted propylene were oxidized with permanganate to produce CO_2 and acetic acid, and the C^{13} content of the CO_2 was measured. It was shown by Fries and Calvin (*5*) that CO_2 so produced comes from the methylene group. Less than 3% of the C^{13} was in the methylene group of the feed propylene.

RESULTS

Compositions of the gaseous fractions analyzed are given in Table 1. Computed results obtained by correcting for the 1.1% natural abundance of C^{13} and for other secondary effects are shown in Table 2. The C^{13} content of the carbonyl group in the acrolein was found to be 50–55% of that of the original methyl group.

DISCUSSION

In the conversion of propylene to acrolein at least two C—H bonds must be broken and a C=O bond must be formed. It is likely that several species more or less strongly bonded to the catalyst surface are involved, including hydrogen atoms, oxygen atoms, and two or more hydrocarbon species. An experiment such as the present one cannot clarify all the steps, but it does supply evidence regarding the initial step. The mechanisms considered as likely are sketched below, where the free bonds are visualized as being attached to the solid surface, and underlining denotes the C^{13}. Isomerization of an allyl intermediate attached to the surface involves an electron shift and attachment of the other end of the intermediate to the surface.

Initial removal of an H atom, no isomerization.

$$\begin{array}{ll} & \text{(1a)} \\ \mathrm{CH_2{=}CH{-}\underline{C}H_3} & \\ \quad\downarrow & \text{(removal of H atom)} \\ \mathrm{CH_2{=}CH{-}\underline{C}H_2{-}} & \\ \quad\downarrow & \text{(addition of O atom)} \\ \mathrm{CH_2{=}CH{-}\underline{C}H_2{-}O{-}} & \\ \quad\downarrow & \text{(removal of H atom)} \\ \mathrm{CH_2{=}CH{-}\underline{C}H{=}O} & \end{array}$$

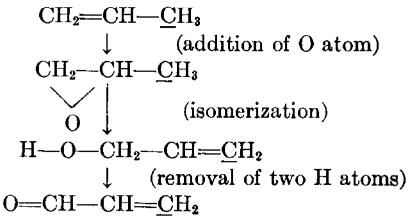
Initial removal of an H atom followed by isomerization.

$$\begin{array}{lcl} \mathrm{CH_2{=}CH{-}\underline{C}H_3} & & \text{(1b)} \\ \quad\downarrow & \text{(removal of H atom)} & \\ & \text{(isomerization)} & \\ \mathrm{CH_2{=}CH{-}\underline{C}H_2{-}} & \rightleftarrows & \mathrm{{-}CH_2{-}CH{=}\underline{C}H_2} \\ \quad\downarrow & \text{(addition of O atom)} & \quad\downarrow \\ \mathrm{CH_2{=}CH{-}\underline{C}H_2{-}O{-}} & & \mathrm{{-}OCH_2{-}CH{=}\underline{C}H_2} \\ \quad\downarrow & \text{(removal of H atom)} & \quad\downarrow \\ \mathrm{CH_2{=}CH{-}\underline{C}H{=}O} & & \mathrm{O{=}CH{-}CH{=}\underline{C}H_2} \end{array}$$

Initial addition of an O atom to double bond.

$$\begin{array}{lll} \mathrm{CH_2{=}CH{-}\underline{C}H_3} & & \text{(2)} \\ \qquad\downarrow & \text{(addition of O atom)} & \\ \mathrm{{-}O{-}CH_2{-}CH{-}\underline{C}H_3} & & \\ \qquad\downarrow & \text{(removal of two H atoms)} & \\ \mathrm{O{=}CH{-}CH{=}\underline{C}H_2} & & \end{array}$$

Initial formation of propylene oxide.



(3)

In mechanisms (2) and (3) we expect no C^{13} in the CHO group, while in mechanism (1a) we expect all the C^{13} in the CHO group. In (1b) half the C^{13} in the acrolein is predicted to be in the CHO group, as observed, and thus the evidence favors this mechanism, with initial removal of a hydrogen atom to form an allyl intermediate which is isomerized rapidly.

Some isomerization of unreacted propylene was observed, and 20% of the recovered material was calculated to be 1-propene-1-C^{13}. Considering the initial content of C^{13} in the methylene position, this corresponds to about 38% of equilibrium isomerization. Such incomplete isomerization alone cannot explain the 50% appearance of C^{13} in the carbonyl group, and the evidence for mechanism (1b) remains valid unless we postulate an unlikely situation. For example, it is conceivable that adsorbed propylene stays on the surface for some time, where all of it is isomerized to equilibrium and most of the adsorbed material is subsequently oxidized to acrolein. This seems unlikely from other evidence concerning isomerization and oxidation reactions on effective solids at about 300°C. Furthermore, the evidence of Adams and Jennings (*2*) is free from this possibility, since they observed very little isomerization of propylene over Cu_2O on Alundum. We have reason to think that the isomerization observed in the present work resulted from independent sites on the acid-washed Celite VIII, and not from the Cu_2O. Thus, we later found that Cu_2O/Celite VIII had much more activity for isomerization of propylene oxide to propionaldehyde than did Cu_2O/Alundum.

Mechanism 3, the initial formation of propylene oxide, is ruled out by the result with C^{13}, and also by independent experiments in which propylene oxide and oxygen were passed over Cu_2O/Celite VIII and over Cu_2O/Alundum. In both cases the major product was propionaldehyde and not acrolein. Propionaldehyde is not a major product in the conversion of propylene to acrolein. Furthermore, propionaldehyde, unlike allyl alcohol, is not readily converted to acrolein.

It is interesting to note that the carbon dioxide by-product from the oxidation of propylene to acrolein was 17.4% $C^{13}O_2$. This is in agreement with $53.5/3 = 17.8\%$ expected if the carbon dioxide comes exclusively from total oxidation of a portion of the acrolein or propylene rather than from selective oxidation of an end carbon. The relative amounts of other by-products also show that most of the CO_2 comes from total oxidation of C_3 compounds. Since selectivity declines with conversion as required for consecutive reactions, it appears that the carbon dioxide is a secondary product formed mainly by complete oxidation of part of the acrolein. A similar conclusion has been reached by others (*6, 7*).

Mass Spectrum of Propylene

The mass spectrum of 1-propene-$3C^{13}$, observed in the course of the studies described in the text of this paper, possesses certain features of pertinent interest to the problem of the origin of mass spectra that are noted in the following paragraphs.

The isotopic assay of the tagged propylene, given in column 2 of Table 1, was made from the mass spectrum of the sample by the methods described previously (*8*), under the assumption that there are no C^{13} isotope effects on the relative intensities of the "C^{13} ions" of the mass spectrum. There are shown in Table 3 the C_2 and C_1 portions of the mass spectra (characteristic of 75 volt ionizing electrons and the ion source at 80°C) of propylene-C_0^{13} and the propylenes $[—C_1^{13} + C_2^{13}]$ of the tagged sample. These spectra were computed in the usual manner from the observed spectra of ordinary propylene and of the tagged sample. The intensities of the ions are shown on the basis of the sum of the intensities of all singly charged ions equal to 100.

TABLE 3

Partial Mass Spectra of Propylenes[a,b]

Ion or m/q	$C_3H_6—C_0^{13}$	Tagged C_3H_6
$[C_3H_6—C_2^{13}]^+$	—	(0.46_1)[c]
$[C_3H_6—C_1^{13}]^+$	—	(20.1_4)
$[C_3H_6—C_0^{13}]^+$	20.6_0	0.0
29^+	0.00	0.13_6
28^+	0.11	3.8_1
27^+	7.54	4.2_6
26^+	1.67	0.9_1
25^+	0.28	0.18
24^+	0.07	0.03
16^+	0.01_0	0.25_0
15^+	0.43_0	0.26_5
14^+	0.21_6	0.18_0
13^+	0.10_0	0.08_5
12^+	0.07_0	0.05_1
Sum (12^+–29^+)	10.4_9	10.1_6

[a] 75 Volt ionizing electrons, 80°C ion source temperature: $\pi/2$-sector analyzer mass spectrometer with magnetic scan.

[b] Sum of intensities of singly charged C_1–C_3 equals 100.0.

[c] Assumed, see text.

From the method of synthesis of the tagged propylene, and the effective enrichment of the methyl iodide-C^{13} employed [as deduced (*8*) from the total C^{13} content of the tagged propylene], the expected species distribution would be, $C_3H_6\text{-}3\text{-}C_1^{13} = 96\%$, $C_3H_6\text{-}2\text{-}C_1^{13} = C_3H_6\text{-}1\text{-}C_1^{13} = 1\%$, and total $C_3H_6\text{-}C_2^{13} = 2\%$. The results of C^{13} assays of the CO_2 and acetate formed in the controlled, selective oxidation of the propylene with dilute $KMnO_4$ solution confirmed the expectation that less than 3% of the C^{13} was in the methylene group of the C^{13}-containing species. Inasmuch as the propylene was in contact with only cool dry glass and/or cool gold-plated metal surfaces prior to exposure to the ionizing electron beam, there is but the remotest possibility that thermal and/or catalytic isomerization of the propylene-3-C_1^{13} could occur prior to ionization. Thus the finding that the abundances of the ions of mass-to-charge ratio equal to 28^+ and 16^+ in the spectrum of the tagged material, respectively, are but about one-half those of the intensities of the ions of $m/q = 27^+$ and 15^+ in the spectrum of C_3H_6-C_0^{13} can be taken as reasonably conclusive evidence that the propylene ions formed by electron (75 ev) impact undergo isomerization in the sense,

$$CH_2 = CH - C^{13}H_3^+ \rightleftarrows CH_3 - CH = C^{13}H_2^+ \quad (4)$$

to essentially equilibrium prior to dissociation as either,

$$C_3H_6^+ \rightarrow C_2H_3^+ + CH_3 \quad (5a)$$

$$C_3H_6^+ \rightarrow C_2H_3 + CH_3^+ \quad (5b)$$

The fact that the intensity of $m/q = 16^+$ (tagged sample) is definitely greater than half that of $m/q = 15^+$ ($-C_0^{13}$) while the intensity of $m/q = 28^+$ (tagged sample) is almost identically half that of $m/q = 27^+$ ($-C_0^{13}$) suggests that whereas the rate of the reaction (5a) of the propylene ion is definitely slower than the isomerization reaction (4), the rate of reaction (5b) is essentially comparable with that of (4). This finding that reaction (5a) is slow compared to reaction (4) of the propylene ion is not unexpected in view of the well known similarity of the intensities of the various C_2 ions of the mass spectra of the three normal butylenes (*9, 10*).

It will be noted that the sum of the intensities of the C_1 and C_2 ions in the mass spectrum of the C^{13}-labeled propylene is 3% less than that found in the C^{13}-free material. This finding suggests there to be a small C^{13} isotope effect reducing the dissociation rates of the propylene-C^{13} ions involving the scission of C–C bonds.

ACKNOWLEDGMENT

Acknowledgment of discussions with C. R. Adams, and T. J. Jennings, of this laboratory, is gratefully recorded.

REFERENCES

1. HEARNE, G. W., AND ADAMS, M. U.S. Patent 2,451,485 (to Shell Development Company) (1948).

2. ADAMS, C. R., AND JENNINGS, T. J., *J. Catalysis* **2,** 63 (1963).

3. SWALLEN, L. C., AND BOORD, C. E., *J. Am. Chem. Soc.* **52,** 651 (1930).

4. VOGE, H. H., AND ATKINS, L. T., *J. Catalysis* **1,** 171 (1962).

5. FRIES, B. A., AND CALVIN, M., *J. Am. Chem. Soc.* **70,** 2235 (1948).

6. ISAEV, O. V., MARGOLIS, L. YA., AND SAZANOVA, I. S., *Proc. Acad. Sci. USSR, Phys. Chem. Sect.* **129,** 905 (Engl. transl.) (1959).

7. ENIKEEV, E. KH., ISAEV, O. V., AND MARGOLIS, L. YA., *Kinetika i Kataliz* **2,** 431 (1960).

8. STEVENSON, D. P., *J. Chem. Phys.* **19,** 17 (1951).

9. DIBELER, V. H., *J. Res. Nat. Bur. Stand.* **38,** 329 (1947).

10. STEVENSON, D. P., *J. Am. Chem. Soc.* **65,** 209 (1943).