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The Vanadium-Pentoxide-Catalyzed Oxidation of Pentenes

II. Straight-Chain Pentenes

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The oxidation of pent-2-ene in the temperature range 250–450°C over a freshly prepared vanadium pentoxide catalyst produces acetaldehyde, propionaldehyde, ethylene, propylene, *trans*-2,3-epoxypentane, acetone, and carbon dioxide. Use of the catalyst for approximately 5 hr causes a marked and sudden change in the pattern of product formation. The oxidation becomes more rapid but much less selective, at least 14 extra products being formed. The oxidation of pent-1-ene under similar conditions proceeds largely via isomerization to pent-2-ene and oxidation of the latter. On a "new" catalyst, the products are probably formed by interaction of adsorbed pentene with O^{2-}. An overall mechanism results in which the catalyst itself is reduced by the adsorbed pentene and re-oxidized by gaseous oxygen. V^{5+} is therefore the active oxidant. On an "old" catalyst, however, gaseous molecular oxygen attacks the adsorbed pentene directly and the oxidation acquires free-radical chain character with resultant loss of selectivity. It is therefore possible to reconcile the apparently contradictory "oxidation–reduction" and "hydroperoxylation" mechanisms for the oxidation of unsaturated hydrocarbons over vanadium pentoxide.

INTRODUCTION

In Part I (*1*), the vanadium-pentoxide-catalyzed oxidation of branched-chain pentenes was described. Each branched-chain pentene isomerized on the catalyst to 2-methylbut-2-ene and the subsequent pattern of oxidation gave products characteristic of this nonterminal pentene. The probable mechanism of oxidation involved reduction of the catalyst by adsorbed fuel and its reoxidation by oxygen, in agreement with the postulates of Mars and van Krevelen (*2*). In order to investigate whether this mechanism is a general one for the oxidation of alkenes over vanadium pentoxide, extensive studies of the corresponding reactions of pent-1-ene and pent-2-ene have been made. The pattern of product formation and its variation with catalyst age, temperature, contact time, and oxygen availability are reported here; the nature of changes during oxidation in the physicochemical properties of the catalyst itself are described in Part III (following paper).

METHODS

The preparation of the pumice-supported vanadium pentoxide catalyst, the apparatus and procedure employed for catalytic studies, and the analytical methods have been described in Part I (*1*).

(*1*) *Preparation and Purification of Pentenes*

(*a*) *Pent-2-ene*

Redistilled pentan-2-ol was dehydrated with 50% (v/v) sulfuric acid, pentene being produced in 87% yield. This product was refractionated with 50% (v/v) sulfuric acid, treated with 5% aqueous sodium hydroxide to remove any sulfur dioxide, dried, and redistilled. The product, which was obtained in 75% overall yield, had a boiling point of 36.2°C and a refractive index ($n_{20}{}^{D}$) of 1.3794 (cf. literature b.p. of pent-2-ene, 36.4°C;

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$n_{20}^{D} = 1.3797$). Gas-liquid chromatographic analysis showed that the impurity content was less than 0.5%. (Pentan-3-ol, a better starting material, was not available in sufficient quantities.)

(*b*) *Pent-1-ene*

Pent-1-ene, obtained commercially, was treated with 5% aqueous sodium hydroxide to remove any sulfur dioxide, dried, and fractionally distilled. The product had a boiling point of 30.2°C and a refractive index (n_{20}^{D}) of 1.3718 (cf. literature b.p. of pent-1-ene, 30.1°C; $n_{20}^{D} = 1.3715$). Gas chromatographic analysis showed that the product contained less than 0.5% of other isomeric pentenes and no other impurity.

(*2*) *Additional Analytical Methods*

Solid products were produced in small quantities during the vanadium-pentoxide-catalyzed oxidation of straight-chain pentenes. The infrared spectra of these were determined using a modification of the Nujol mull method (*3*). Discs of pure potassium bromide and of 0.1–0.5% of the sample in potassium bromide were prepared by placing these solids in cylindrical steel dies, evacuating the air, and then increasing the pressure to 10 000 lb. inch^{-2}. Infrared spectra were obtained using a Perkin-Elmer Infracord apparatus (Model 137).

Results

(*1*) *The Vanadium-Pentoxide-Catalyzed Oxidation of Pent-2-ene*

(*a*) *The Effect of Catalyst Age*

The course of oxidation of pent-2-ene over 8–10 mesh (B.S.) pumice-supported vanadium pentoxide is highly dependent upon the "age" of the catalyst, i.e., upon the time for which it has been in contact with a reacting pentene-oxygen-nitrogen mixture. A marked and sudden change in the pattern of product formation occurs after a period the length of which is dependent upon the oxygen-to-pentene ratio and the contact time. During the reaction of pent-2-ene with 1.25 times its own molar quantity of oxygen at a contact time of 33.6 sec, for example, the change occurs after approximately 5 hr of use. The catalyst subsequently has a considerably higher activity but the oxidation becomes much less selective. Subdivision of the results into those over a "new" catalyst (less than 5 hr old) and those over an "old" catalyst is therefore necessary.

(*b*) *The Effect of Temperature*

The lowest temperature at which appreciable oxidation of pent-2-ene occurs over an "old" vanadium pentoxide catalyst supported on 8–10 mesh pumice is about 250°C (Fig. 1). The isomers *cis*-pent-2-ene and *trans*-pent-2-ene behave identically both in susceptibility to oxidation and in the natures and amounts of products formed. Acetaldehyde, propionaldehyde, ethylene, propylene, *trans*-2,3-epoxypentane, acetone, and carbon dioxide are the products, acetaldehyde being by far the major one. As the temperature is raised, the consumption of pent-2-ene increases sharply, and the amounts of oxygenated products and of lower alkenes show corresponding increases. At temperatures above 300°C considerable quantities of methanol, *n*-butyraldehyde, butanone, pentan-2-one, and pentan-3-one, and small amounts of C_{10} hydrocarbons, crotonaldehyde, ethanol, butan-2-ol, ethylene oxide, propylene oxide, 2-methyl-2,3-epoxypropane, *trans*-2,3-epoxybutane, and 3-methylbutan-2-one are produced also. (For clarity, many of the minor products are not shown in Fig. 1.) Of these products, only ethylene, propylene, and butanone are resistant to further increase of temperature.

On a "new" catalyst, the products of oxidation at low temperatures (<300°C) are similar to those on an "old" catalyst, acetaldehyde being the major product. As the temperature is increased, the amounts of these increase but, in contrast to the behavior on an "old" catalyst, the oxidation does not become less selective until the temperature approaches 400°C.

The effect of temperature on the gas-phase oxidation of pent-2-ene under similar conditions of oxygen availability and residence time has been studied for comparative purposes and is shown in Fig. 2. Appreciable

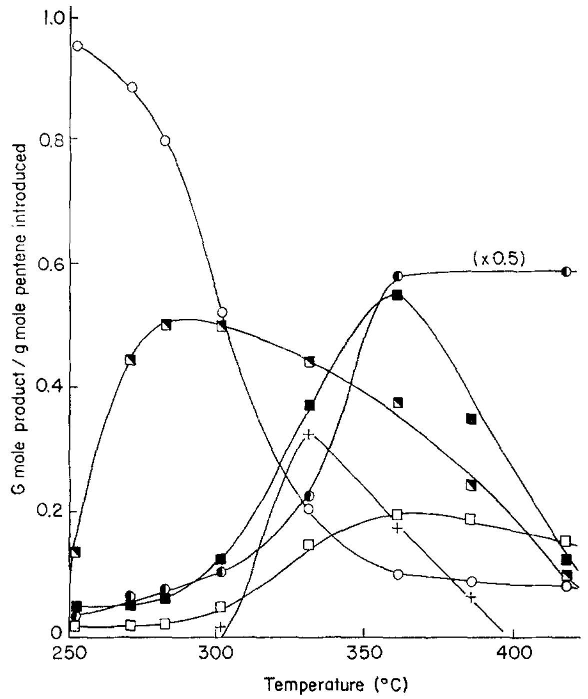


FIG. 1(a)

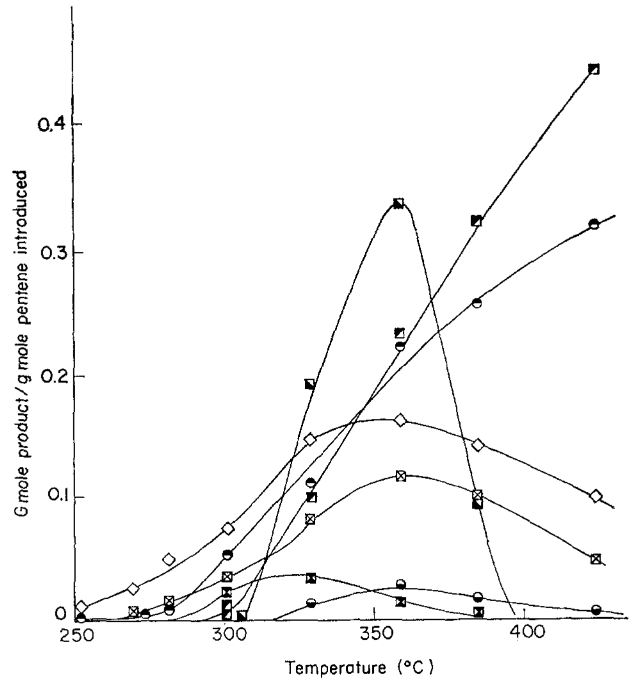


FIG. 1(b)

FIG. 1. The oxidation of pent-2-ene on an "old" catalyst: the effect of temperature (contact time, 33.6 sec; oxygen:pentene = 1.25): (a) ○, pent-2-ene; ◪, acetaldehyde; ■, propionaldehyde; +, methanol; ◐, ethylene (×0.5); □, acetone; (b) ◩, n-butyraldehyde; ◪, butanone; ◓, propylene; ◇, *trans*-2,3-epoxypentane; ⊠, pentan-2-one + pentan-3-one; ◒, C_{10} hydrocarbons; ⧗, crotonaldehyde.

oxidation occurs at about 275°C, producing acetaldehyde and propionaldehyde. The variations with temperature of the amounts of these products are closely similar, in marked contrast to the vanadium-pentoxide-catalyzed oxidation. Methane, methanol, *trans*-2,3-epoxypentane, acetone, ethylene, pentan-2-one, pentan-3-one, and butanone are the additional products at higher temperatures, particularly large amounts of methane being produced. No C_{10} hydrocarbons or *n*-butyraldehyde were found in the absence of the catalyst, but organic peroxides were formed in small quantities.

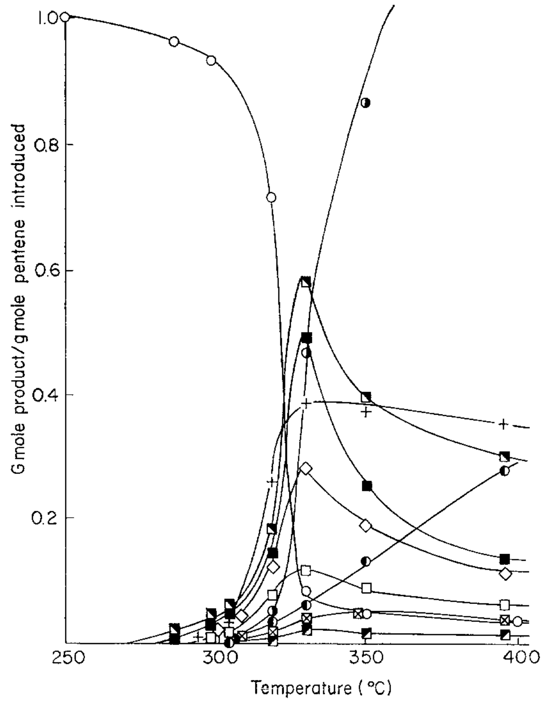


FIG. 2. The oxidation of pent-2-ene in the gas phase: the effect of temperature (residence time, 33.6 sec; oxygen:pentene = 1.25): ○, pent-2-ene; ◑, methane; ,◪ acetaldehyde; ■, propionaldehyde; +, methanol; ◇, *trans*-2,3-epoxypentane; □, acetone; ◐, ethylene; ⊠, pentan-2-one + pentan-3-one; ◩, butanone.

(*c*) *The Effect of Contact Time*

(i) Using a "new" catalyst. On a "new" catalyst, the products of oxidation of pent-2-ene at 300°C are acetaldehyde, propionaldehyde, acetone, ethylene, propylene, *trans*-2,3-epoxypentane, pent-1-ene, and carbon dioxide, of which the first four are the major products (Fig. 3). The concentration of each of these increases with contact time in the range 0–30 sec; ethylene, acetone, pent-1-ene, and *trans*-2,3-epoxypentane are largely unaffected by a further increase but the concentrations of acetaldehyde, propylene, and propionaldehyde pass through definite maxima. (Stated contact times refer to the total time for which the gases are in contact with the catalyst, of which the total area was about 50 m^2. Catalyst surface areas are discussed in Part III.)

(ii) On an "old" catalyst. The consumption of pent-2-ene on an "old" catalyst is considerably greater than on a "new" catalyst under the same conditions. At 300°C with an oxygen-to-pentene ratio of 1.25, the amounts of acetaldehyde, propionaldehyde, and acetone formed on each catalyst are similar (Fig. 4). On an "old" catalyst, however, only very small amounts of ethylene and propylene are produced and little pent-1-ene remains, but carbon dioxide is formed in far larger amounts. The C_5 epoxide is less stable on an "old" catalyst than on a "new" catalyst. Many products are formed on an "old" catalyst which were absent on a "new" catalyst. These include methanol (in large amounts) and (in small quantities) ethylene oxide, propylene oxide, 3-methylbutan-2-one, 2-methyl-2,3-epoxypropane, *trans*-2,3-epoxybutane, pentan-2-one, pentan-3-one, crotonaldehyde, butanone, ethanol, and butan-2-ol. The variations with contact time of the concentrations of each of these are shown in Fig. 4.

Very small amounts of solid products are also produced; infrared spectroscopic analysis has shown that the major constituent of these is maleic acid ($cis\text{-}HO_2CCH{=}CHCO_2H$) and that crotonic acid ($trans\text{-}CH_3CH{=}CHCO_2H$) and citraconic acid [$cis\text{-}HO_2C(CH_3){=}CHCO_2H$] are also present.

(*d*) *The Effect of Oxygen Availability*

The availability of gaseous oxygen was varied from zero to three times the molar concentration of fuel and the effect on product formation at 300°C on both "new" and "old" catalysts was determined.

(i) On a "new" catalyst. On a "new" vanadium pentoxide catalyst at 300°C, in

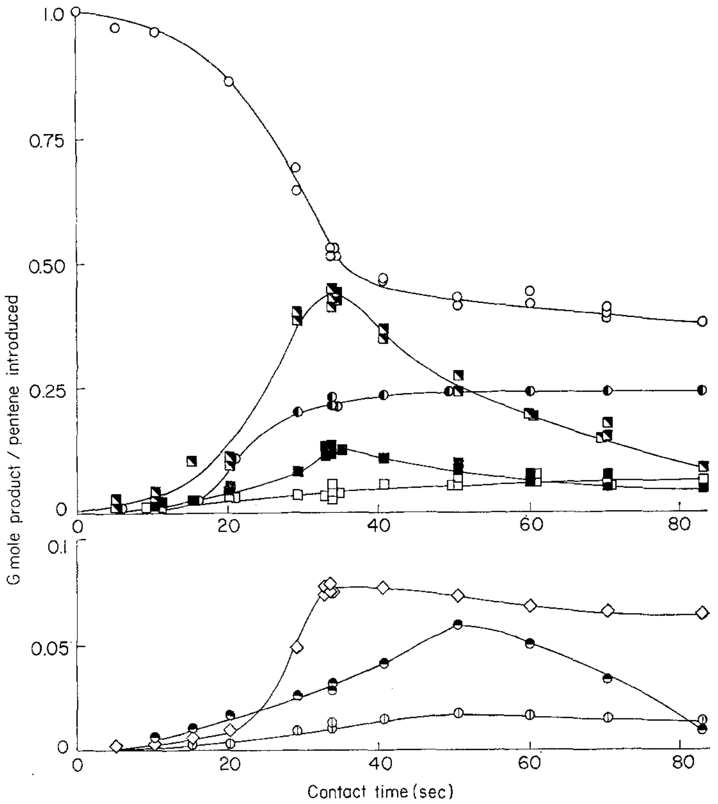


FIG. 3. The oxidation of pent-2-ene on a "new" catalyst: the effect of contact time (temperature, 300°C; oxygen:pentene = 1.25): ○, pent-2-ene; ◪, acetaldehyde; ◐, ethylene; ■, propionaldehyde; □, acetone; ◇, *trans*-2,3-epoxypentane; ◓, propylene; ⦶, pent-1-ene.

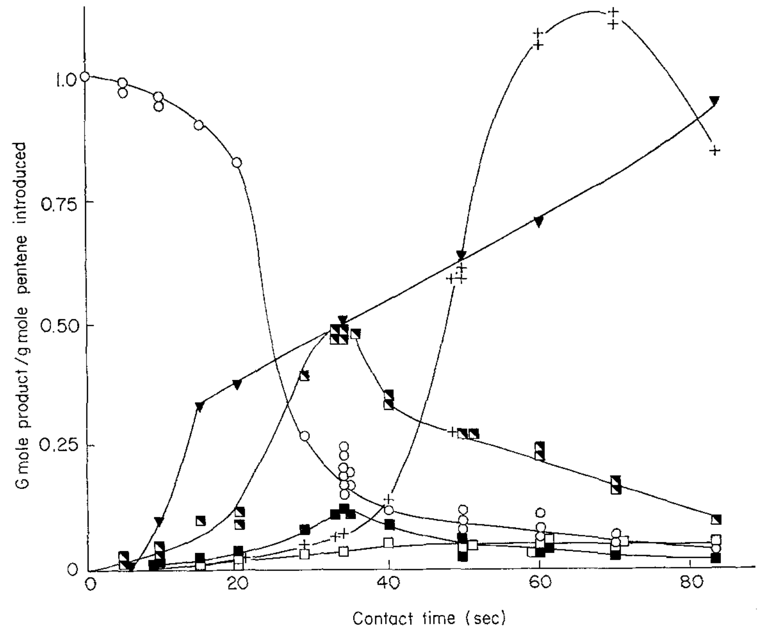


FIG. 4(a)

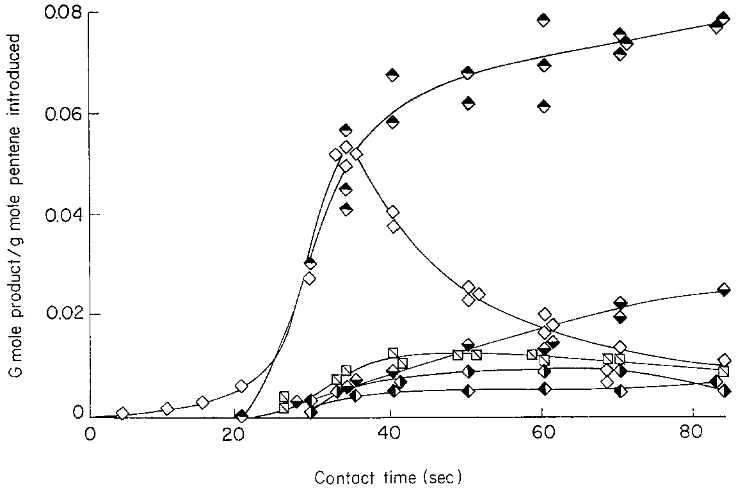


FIG. 4(b)

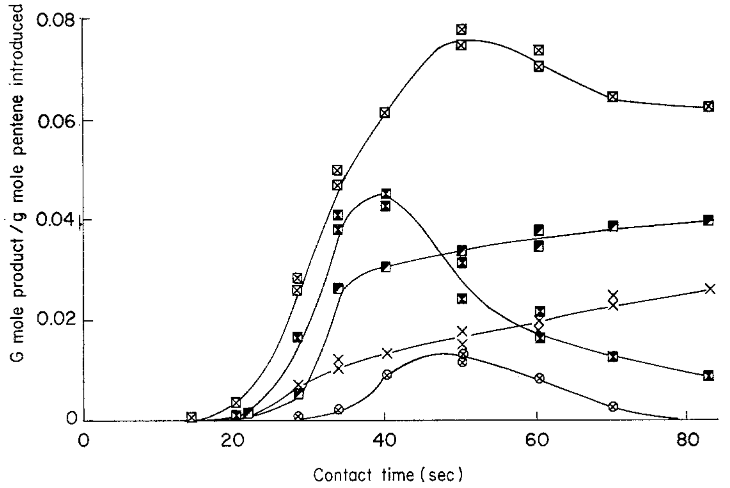


FIG. 4(c)

FIG. 4. The oxidation of pent-2-ene on an "old" catalyst: the effect of contact time (temperature, 300°C; oxygen:pentene = 1.25). (a) Major products: ○, pent-2-ene; ▼, carbon dioxide; ◪, acetaldehyde; ■, propionaldehyde; □, acetone; +, methanol. (b) Minor products: ⬘, ethylene oxide; ◇, *trans*-2,3-epoxypentane; ⧅, 3-methylbutan-2-one; ⬗, *trans*-2,3-epoxybutane; ⬖, 2-methyl-2,3-epoxypropane; ⬙, propylene oxide. (c) Minor products: ⊠, pentan-2-one + pentan-3-one; ⧗, crotonaldehyde; ◩, butanone; ×, butan-2-ol; ⊗, ethanol.

the absence of any gaseous supply of oxygen, pent-2-ene is converted to about 4 mole % of propylene, about 1 mole % of each of ethylene and pent-1-ene, and smaller quantities of acetaldehyde and propionaldehyde. The introduction of gaseous oxygen leads to the formation of *trans*-2,3-epoxypentane and to a rapid increase in the amount of ethylene formed, but does not substantially affect the amounts of the other products until the oxygen-to-pentene ratio is about 0.5 (Fig. 5). Further increase in oxygen availability, however, leads to the increased production of oxygenated products and, successively, to their further oxidation.

(ii) On an "old" catalyst. In the absence of gaseous oxygen over an "old" catalyst the only product is pent-1-ene (in very small amounts). The introduction of gaseous oxygen leads, however, to the rapid oxida-

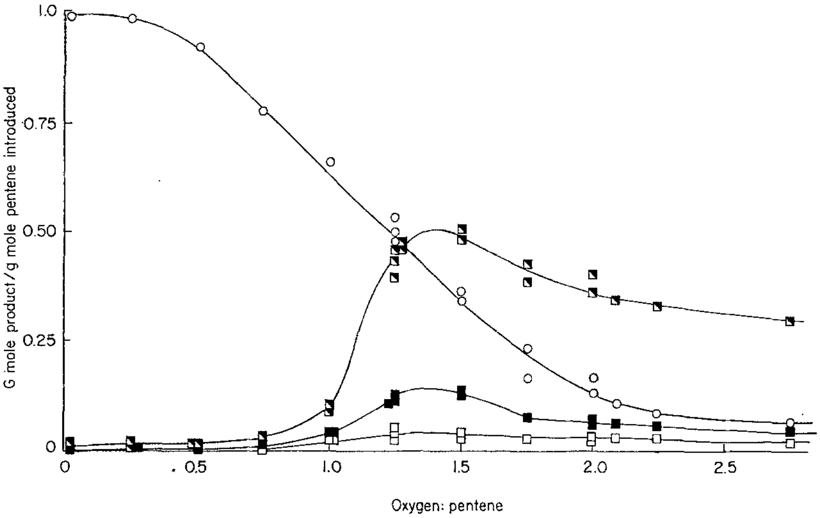


FIG. 5(a)

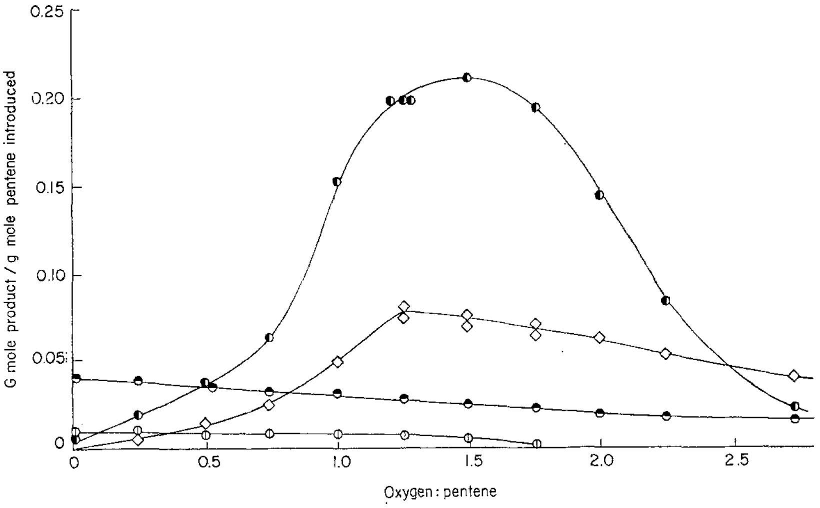


FIG. 5(b)

FIG. 5. The oxidation of pent-2-ene on a "new" catalyst: the effect of oxygen:pentene ratio (temperature, 300°C; contact time, 33.6 sec). (a) Major products: ○, pent-2-ene; ◨, acetaldehyde; ■, propionaldehye; □, acetone. (b) Minor products: ◐, ethylene; ◓, propylene; ⦶, pent-1-ene; ◇, *trans*-2,3-epoxypentane.

tion of pent-2-ene to more than 20 different products (Fig. 6), of which acetaldehyde, propionaldehyde, methanol, and carbon dioxide are the major ones. At long contact times, considerable amounts of acids are produced.

(e) The Carbon Balance

Carbon balances for the oxidation of pent-2-ene at 300°C on "new" and "old" vanadium pentoxide catalysts are shown in Tables 1 and 2, respectively. In all cases, the total carbon output is near to 100% of the carbon input.

(2) The Vanadium-Pentoxide-Catalyzed Oxidation of Pent-1-ene

The oxidation of pent-1-ene was studied at 300°C on an "old" catalyst. Under these

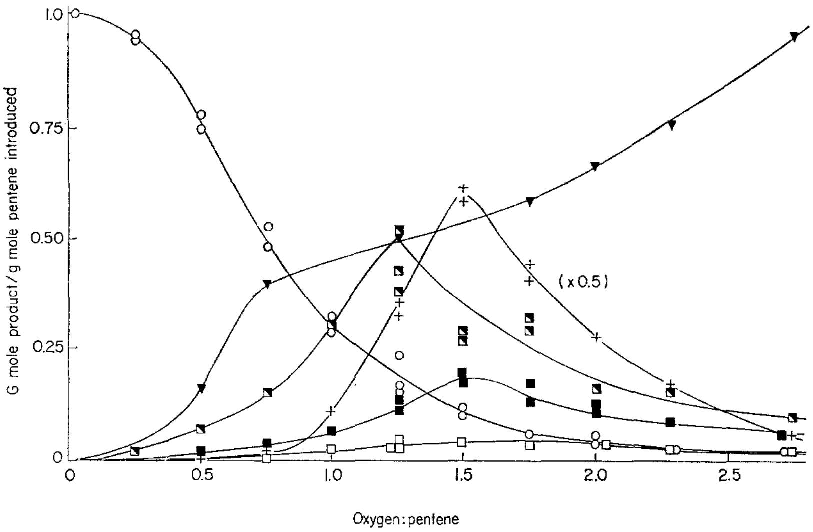


FIG. 6(a)

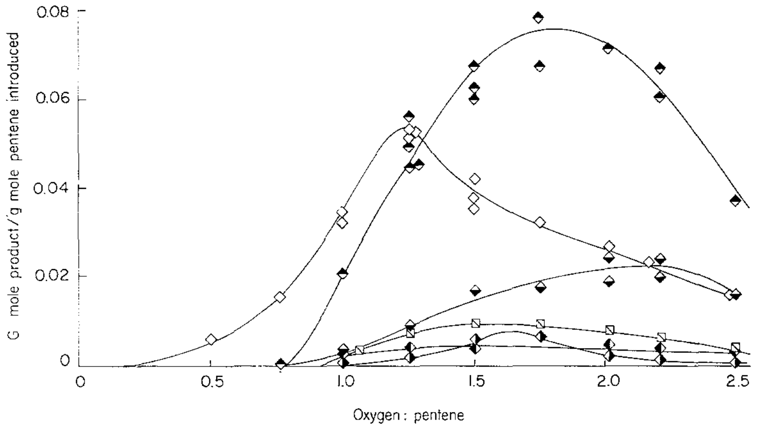


FIG. 6(b)

FIG. 6. The oxidation of pent-2-ene on an "old" catalyst: the effect of oxygen:pentene ratio (temperature, 300°C; contact time, 33.6 sec). (a) Major products: ○, pent-2-ene; ▼, carbon dioxide; ◪, acetaldehyde; ■, propionaldehyde; □, acetone; +, methanol (×0.5). (b) Minor products: ◇, *trans*-2,3-epoxypentane; ⬘, ethylene oxide; ⧄, 3-methylbutan-2-one; ⬙, propylene oxide; ⬗, 2-methyl-2,3-epoxypropane; ⬖, *trans*-2,3-epoxybutane. (c) Minor products: ⊠, pentan-2-one + pentan-3-one; ⧗, crotonaldehyde; ◩, butanone; ×, butan-2-ol; ⊗, ethanol.

conditions, extensive isomerization to pent-2-ene occurs and the oxidation products are qualitatively similar to those produced from the latter pentene (Table 3). Results obtained on a "new" catalyst lead to a similar conclusion.

The effect of temperature on the gas-phase oxidation of pent-1-ene was studied for comparative purposes. In this regime, oxidation of pent-1-ene becomes appreciable at 260°C, (Fig. 7). The major products are methane, ethylene, *n*-butyraldehyde, formaldehyde, acetaldehyde, butanone, and methanol, and minor products include 3-methylpentan-2-one, acetone, and propionaldehyde. The relative yields of products contrast with those from the catalyzed oxidation.

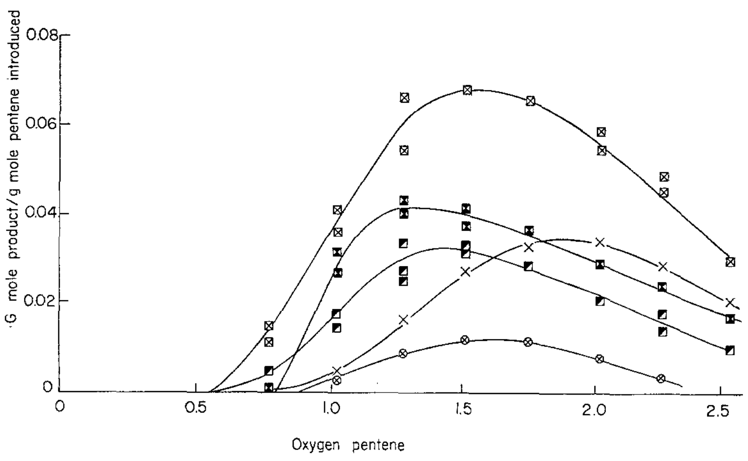


Fig. 6(c)

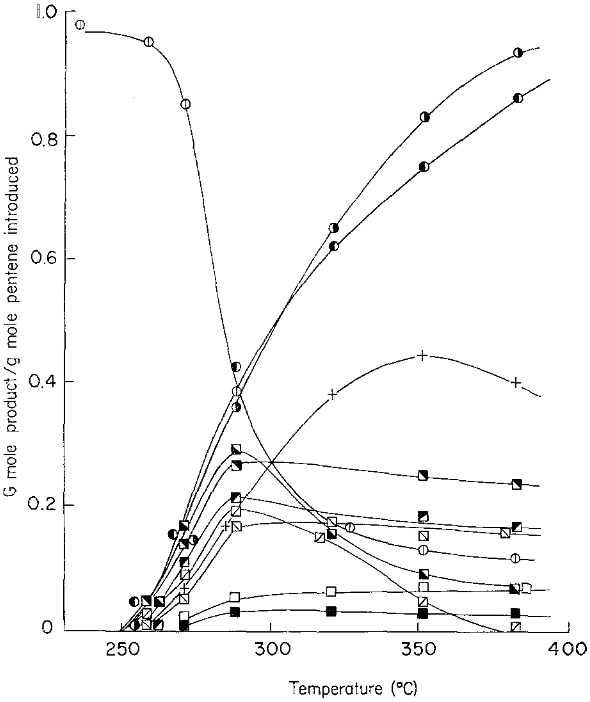


Fig. 7. The oxidation of pent-1-ene in the gas phase: the effect of temperature (contact time, 33.6 sec; oxygen:pentene = 1.25): ⦶, pent-1-ene; ◐, ethylene; ◑, methane; ◪, *n*-butyraldehyde; ◩, acetaldehyde; ⬔, butanone; □, acetone; +, methanol; ⧅, 3-methylbutan-2-one; ⧄, formaldehyde; ■, propionaldehyde.

(3) The Isomerization of Straight-Chain Pentenes on Vanadium Pentoxide

It is evident that isomerization of pent-1-ene to pent-2-ene is an important factor in the catalytic oxidation of the former and that the reverse process occurs to a smaller extent in the oxidation of the latter. Studies of the isomerization of straight-chain pentenes in the absence of oxygen at 300°C both on the catalyst and in the gas phase have therefore been made. On a "new" catalyst, 5.3% of pent-1-ene isomerizes

TABLE 1

Carbon Balance: The Oxidation of Pent-2-ene on a "New" Catalyst

Carbon input, 1.02 × 10^{-3} g-atoms/min
Oxygen:pentene = 1.25 Temperature, 300°C

Contact time (sec): Carbon output (% of carbon input)	15.0	33.6	60.0
Pent-2-ene	94.2	53.0	41.7
Acetaldehyde	2.8	19.9	9.2
Acetone	0.4	2.2	3.7
Propionaldehyde	1.1	7.5	4.5
C_2 hydrocarbons	1.5	9.0	10.4
C_3 hydrocarbons	0.5	2.0	3.2
C_5 epoxide	0.5	7.7	7.6
Carbon dioxide	0.2	0.9	9.1
Total	101	102	89

to pent-2-ene, giving approximately equal amounts of *cis* and *trans* isomers (Table 4). Appreciable quantities of branched-chain pentenes are also produced. Both *cis*-pent-2-ene and *trans*-pent-2-ene rapidly isomerize on the catalyst to give 58.8% of the *trans* isomer and 37.9% of the *cis* isomer; 1.6% of pent-1-ene and a similar quantity of C_{10} hydrocarbons are produced but only very small quantities of branched-chain pentenes are formed.

TABLE 2

Carbon Balance: The Oxidation of Pent-2-ene on an "Old" Catalyst

Carbon input, 1.02 × 10^{-3} g-atoms/min
Oxygen:pentene = 1.25 Temperature, 300°C

Contact time (sec): Carbon output (% of carbon input)	15.0	33.6	60.0
Pent-2-ene	84.0	21.0	7.8
Acetaldehyde	3.6	19.2	8.9
Propionaldehyde	1.2	7.2	4.0
Acetone	0.4	1.6	3.3
Methanol	—	1.2	21.0
Crotonaldehyde	—	0.3	1.4
Butanone	—	2.2	2.8
Butan-2-ol	—	0.8	1.4
C_5 epoxide	0.33	5.2	1.7
C_4 epoxides	0.16	0.2	0.4
C_3 epoxide	—	0.6	0.9
C_2 epoxide	—	2.0	2.9
Ethanol	—	0.2	2.3
Pentanones	—	6.4	6.6
C_3 hydrocarbons	0.7	1.8	3.0
C_2 hydrocarbons	1.3	8.8	9.1
Carbon dioxide	7.1	9.4	13.9
Acids + anhydrides	0.1	9.8	10.4
Total	99	98	102

TABLE 3

A Comparison of the Oxidation of Straight-Chain Pentenes over Vanadium Pentoxide[a]

Product	Yield (mole %) based on pentene introduced From pent-1-ene	From pent-2-ene
Ethylene	3.5	Trace
Propylene	1.5	Trace
Pent-1-ene	6	1
Pent-2-ene	1.5	19
C_{10} hydrocarbons	5	Trace
Acetaldehyde	66	51
Propionaldehyde	8	12
n-Butyraldehyde	6	Trace
Acetone	16.5	3.5
Butanone	10	3
Pentanones	3	7
Methanol	21	36
2,3-Epoxypentane	4.5	5.5
Lower epoxides	2	5.5
Ethanol	Trace	1
Butan-2-ol	Trace	1.5
Crotonaldehyde	Trace	4

[a] "Old" catalyst; oxygen:olefin = 1.25; contact time, 33.6 sec; temperature, 300°C.

In the gas phase, by contrast, pent-1-ene gives no pent-2-ene although 2.3% of 3-methylbut-1-ene is formed (Table 4). The *cis* and *trans* isomers of pent-2-ene again give an isomeric mixture but only 0.1% of pent-1-ene and 0.3% of 3-methylbut-1-ene are produced.

Discussion

The oxidation of pent-1-ene over vanadium pentoxide leads to acetaldehyde as the major oxygenated product and gives other products characteristic of the carbon skeleton of pent-2-ene (Table 3). In contrast, the gaseous oxidation of pent-1-ene gives large amounts of *n*-butyraldehyde and formaldehyde (Fig. 7). Despite the fact that pent-1-ene is oxidized rapidly in the gas

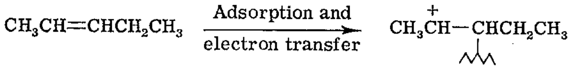
TABLE 4
THE ISOMERIZATION OF STRAIGHT-CHAIN PENTENES[a]

Products	Pentene introduced		
	Pent-1-ene	*trans*-Pent-2-ene	*cis*-Pent-2-ene
(*a*) *On a new vanadium pentoxide catalyst*			
Pent-1-ene	91.0	1.6	1.6
trans-Pent-2-ene	2.6	58.8	58.8
cis-Pent-2-ene	2.7	37.9	37.9
2-Methylbut-1-ene	0.1		
2-Methylbut-2-ene	1.9		
3-Methylbut-1-ene	2.2	0.1	0.1
C_{10} hydrocarbons		1.6	1.6
Total	100.5	100.0	100.0
(*b*) *In the gas phase*			
Pent-1-ene	97.5	0.1	0.1
trans-Pent-2-ene		57.3	57.3
cis-Pent-2-ene		42.2	42.2
2-Methylbut-1-ene	0.1		
3-Methylbut-1-ene	2.3	0.3	0.3
Total	99.9	99.9	99.9

[a] Temperature, 300°C; contact time, 33.6 sec; feedstock of pentene and nitrogen only.

phase at 300°C, the absence from the products of its V_2O_5-catalyzed oxidation of formaldehyde and methane and the low yield of *n*-butyraldehyde show that, in the presence of the catalyst, little gas-phase reaction occurs. It is evident that, on the catalyst, pent-1-ene isomerizes to pent-2-ene and that the latter is subsequently oxidized. The isomerization of pent-1-ene on the catalyst in the absence of oxygen supports this conclusion. The heterogeneous catalytic oxidation of pent-2-ene is representative, therefore, of the oxidations of both straight-chain pentenes, just as the corresponding reaction of 2-methylbut-2-ene is representative of those of branched-chain pentenes (*1*). The pattern of reaction of pentene-oxygen mixtures over vanadium pentoxide involves isomerization of terminal pentenes to nonterminal pentenes and subsequent oxidation of the latter. The reverse isomerization of nonterminal to terminal pentenes occurs to a minor extent.

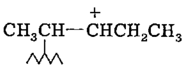
On a "new" catalyst, oxidation of pent-2-ene produces acetaldehyde, propionaldehyde, ethylene, propylene, *trans*-2,3-epoxypentane, acetone, and pent-1-ene. The epoxide, aldehydes, and lower olefins are characteristic of addition of oxygen at the double bond of the pent-2-ene. Although, in general the natures of the products are comparable with those of the major products of the gas-phase oxidation, there are striking quantitative differences between the courses of oxidation in the two régimes. In particular, over the catalyst no methane is formed and the concentrations of acetaldehyde and propionaldehyde are far from equimolar even at low temperatures and low contact times. It is unlikely, then, that attack of the pentene by molecular oxygen plays a major role, a conclusion substantiated by the occurrence, in addition to isomerization, of true oxidation of pent-2-ene on a "new" catalyst in the absence of any gaseous supply of oxygen. It appears that the adsorbed fuel reacts with the oxygen of the "new" catalyst itself (i.e., with O^{2-}) to give carbonyl and olefinic scission products and *trans*-2,3-epoxypentane, the course of oxidation being similar to that of 2-methylbut-2-ene (*1*). Oxidative adsorption of pent-2-ene by donation to V^{5+} of a π electron, resulting in opening of the π bond, gives surface-bonded cations



$$CH_3CH{=}CHCH_2CH_3 \xrightarrow[\text{electron transfer}]{\text{Adsorption and}} CH_3\overset{+}{C}H{-}CHCH_2CH_3$$

(I)

and



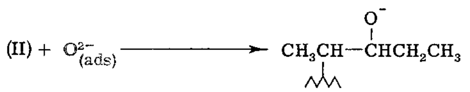
$$CH_3CH{-}\overset{+}{C}HCH_2CH_3$$

(II)

which will react with O^{2-} to produce surface-bonded anions

$$(I) + O^{2-}_{(ads)} \longrightarrow CH_3\overset{O^-}{\overset{|}{C}}-CHCH_2CH_3$$

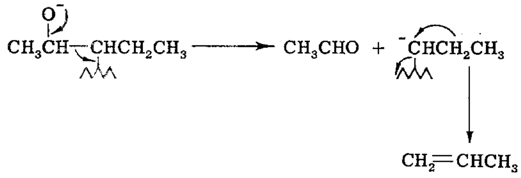
(III)



$$(II) + O^{2-}_{(ads)} \longrightarrow CH_3\overset{O^-}{\overset{|}{CH}}-CHCH_2CH_3$$

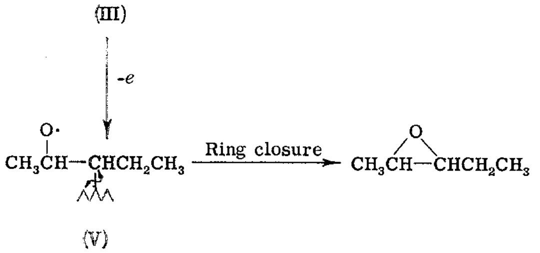
(IV)

The breakdown of (III) gives acetaldehyde and propylene



$$CH_3\overset{O^-}{CH}-CHCH_2CH_3 \longrightarrow CH_3CHO + {}^-CHCH_2CH_3 \longrightarrow CH_2{=}CHCH_3$$

whereas if (III) loses an electron to the surface without scission of the C–C bond, 2,3-epoxypentane is produced

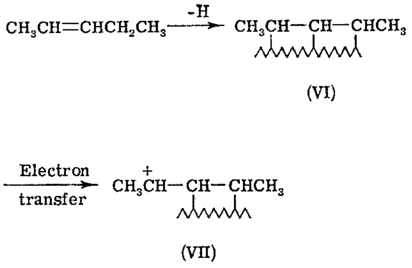


$$(III) \xrightarrow{-e} CH_3\overset{O\cdot}{\overset{|}{CH}}-CHCH_2CH_3\ (V) \xrightarrow{\text{Ring closure}} CH_3CH-CHCH_2CH_3$$

Similar reactions of (IV) produce propionaldehyde, ethylene, and 2,3-epoxypentane. The absence from the products of oxidation of pent-2-ene at 300°C over a "new" catalyst of pentanones, shows that isomerization of the C_5 epoxide does not occur and that H shift in the adsorbed alkoxy radical (V) does not compete effectively with ring closure, in contrast to the course of oxidation of branched-chain pentenes under similar conditions.

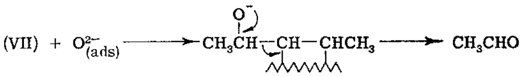
A mechanism of oxidation of straight-chain pentenes over a "new" vanadium pentoxide catalyst analogous to that of branched-chain pentenes accounts qualitatively therefore for all the products except acetone. It is unlikely that the considerable quantities of this product arise by isomerization of pent-2-ene via pent-1-ene to 2-methylbut-2-ene (the direct isomerization does not occur). Acetone may arise from the isomerization of propionaldehyde or by alternative decomposition reactions of the adsorbed anions (III) and (IV).

A significant quantitative difference between straight-chain and branched-chain pentenes is the striking preponderance of acetaldehyde over propionaldehyde in the products of oxidation of pent-2-ene (particularly at low temperatures). Even if acetone is formed by isomerization of propionaldehyde or by reactions of the adsorbed anion (IV) other than those giving propionaldehyde, the preponderance of acetaldehyde is not accounted for. The presence of secondary hydrogen in the allylic position in the pent-2-ene molecule, in contrast to 2-methylbut-2-ene, which has primary allylic hydrogen only, means that the transfer to the surface of hydrogen will be easier in the former case. A π-allylic intermediate (VI) will result (*4*), electron transfer from which will give the cation (VII)



$$CH_3CH{=}CHCH_2CH_3 \xrightarrow{-H} CH_3CH-CH-CHCH_3\ (VI) \xrightarrow[\text{transfer}]{\text{Electron}} CH_3\overset{+}{CH}-CH-CHCH_3\ (VII)$$

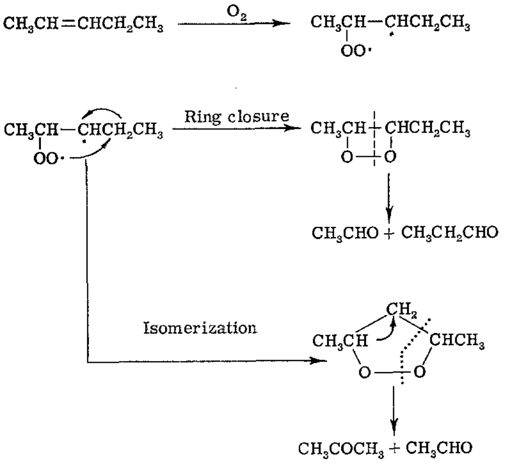
Reaction of this cation with O^{2-} and breakdown of the resulting surface-bonded anion will give acetaldehyde exclusively



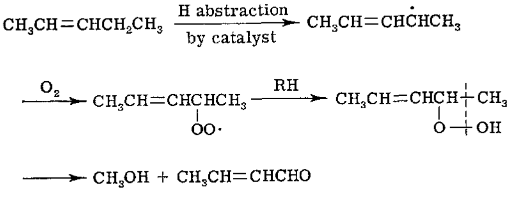
$$(VII) + O^{2-}_{(ads)} \longrightarrow CH_3\overset{O^-}{CH}-CH-CHCH_3 \longrightarrow CH_3CHO$$

Such a sequence of reactions may thus afford an explanation for the preponderance of this product.

On an "old" unselective catalyst, the mechanism evidently differs considerably from that on a "new" catalyst. Although the carbonyl compounds characteristic of a "new" catalyst are still formed, the corresponding lower alkenes are present in trace quantities only and a wide range of other species is also produced. In the absence of gaseous oxygen no oxidation occurs on an "old" catalyst, suggesting that, in contrast to a "new" catalyst, gaseous oxygen is the active oxidant. Acetaldehyde, propionaldehyde, and acetone may therefore be produced by addition of molecular oxygen at the double bond to give a biradical which either cyclizes directly (*5*) or isomerizes (*6*)



The formation of straight-chain pentanones appears to involve isomerization of 2,3-epoxypentane or H shift in the precursor surface-bonded alkoxy radicals, as the maximum yield of these ketones occurs in the contact time range in which the concentration of the epoxide is falling rapidly (Fig. 4). Methanol is formed in very large amounts when the catalyst is unselective and is most easily accounted for on the basis of a hydroperoxylation mechanism similar to that postulated for the vanadium-pentoxide-catalyzed oxidation of butenes (*7*)



$$CH_3CH{=}CHCH_2CH_3 \xrightarrow[\text{by catalyst}]{\text{H abstraction}} CH_3CH{=}CH\dot{C}HCH_3$$

$$\xrightarrow{O_2} CH_3CH{=}CH\underset{\substack{|\\ OO\cdot}}{C}HCH_3 \xrightarrow{RH} CH_3CH{=}CH\underset{\substack{|\\ O}}{C}H\text{-}\!\!\!\!\underset{\substack{\\ \text{-}OH}}{}CH_3$$

$$\longrightarrow CH_3OH + CH_3CH{=}CHCHO$$

This scheme has the merit of accounting also for the small quantities of crotonaldehyde produced. Although these are far from equivalent to those of methanol, it is likely that extensive further oxidation of crotonaldehyde occurs. Methanol may arise also from the free-radical chain oxidation of acetaldehyde, which does not occur during the oxidation at about 300°C of pentenes on "new" catalysts but does in the gas phase at similar temperatures (*5*, *6*).

The further oxidation of crotonaldehyde could account for the formation of maleic acid and crotonic acid. Similarly, ethylene oxide and propylene oxide may arise by further oxidation of ethylene and propylene and *n*-butyraldehyde by the oxidation of the small quantities of pent-1-ene produced by isomerization. Any attempt, however, to explain in detail the minor products formed on an "old" unselective catalyst must of necessity be highly speculative.

The unselective nature of the oxidation on an "old" catalyst, which is comparable with that of oxidations in the gas phase, strongly suggests that a free-radical chain mechanism operates. It is probable that, under these conditions, the lattice species V^{5+} is now much less important as an oxidant and molecular oxygen is more important. Reduction of V^{5+} to V^{4+} would be expected to lead to such an effect; this will be discussed further in Part III.

The present studies provide, therefore, a correlation between the apparently contradictory "oxidation–reduction" (*2*) and "hydroperoxylation" (*7*) mechanisms for the oxidation of unsaturated hydrocarbons over vanadium pentoxide. On a "new" catalyst, it is likely that oxidation of adsorbed alkene by V^{5+} and reaction of cations so formed with O^{2-} leads to reasonable selective oxidation in which the catalyst is reduced. The role of gaseous oxygen is to reoxidize the catalyst and this step is probably rate-determining (*2*). If this is indeed so, the catalyst will gradually be reduced and its properties would be expected to change (*8*, *9*, *10*), as is indeed found to be the case in the present studies. On an "old" catalyst, molecular oxygen becomes the active oxidizing species, reacting with the fuel directly. The resulting pattern of oxidation is far less selective than that on a new catalyst and probably involves free-radical chain mechanisms similar to those operative during the low-temperature gas-phase oxidation of alkenes (*5*, *6*, *11–14*).

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