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The Vanadium-Pentoxide–Catalyzed Oxidation of Pentenes

I. Branched-Chain Pentenes

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The vanadium-pentoxide–catalyzed oxidation of each of the three branched-chain pentenes in the temperature range 200–400°C produces acetaldehyde, acetone, 2,3-epoxy-2-methylbutane, and 3-methylbutan-2-one as major products. Isomerization of each pentene to 2-methylbut-2-ene is followed by the oxidation of the latter. The active oxidant is not gaseous molecular oxygen; the major products are probably formed by the interaction of adsorbed pentene with the anion O^{2-}. An over-all mechanism results in which the catalyst itself is reduced by the adsorbed pentene and reoxidized by oxygen.

INTRODUCTION

The oxidation of olefins by reaction with molecular oxygen over metal oxide catalysts leads to a wide variety of products. Saturated and unsaturated carbonyl compounds, dienes, epoxides, acid anhydrides, and alcohols are produced, the pattern of their formation being a sensitive function of the exact nature of the catalyst and of the experimental conditions. Several of these products are very useful as starting materials for the production of important industrial chemicals.

The mechanism of catalytic oxidation has been elucidated, however, only in broad outline. It is established that oxygen is adsorbed on metal oxides by an electron-transfer process, giving oxygen anions (*1, 2*) and that olefins are adsorbed due to the donation of an electron from the π bond of the olefin, resulting in the opening of this bond, to give cationic surface species (*3, 4*). The subsequent reactions of these species are complex, however. Oxygen may initially remove allylic hydrogen, as is established during the conversion of propylene to acrolein over cuprous oxide or bismuth molybdate and of butenes to butadiene on similar catalysts (*5, 6, 7*). Alternatively, oxygen may add to the opened π bond, as must be the case during the oxidation of ethylene (*8*). During the oxidation of four-carbon olefins over vanadium pentoxide it is considered (*9*) that initial abstraction of hydrogen is followed by peroxidation of the radical so formed by gaseous molecular oxygen. A surface oxygen species is not, therefore, the active oxidant, the over-all mechanism resembling closely that operative during the autoxidation of olefins. It is difficult to reconcile such a mechanism, however, with the observations by Mars and van Krevelen (*10*) of the production of anthraquinone from anthracene over vanadium pentoxide in the absence of any gaseous source of oxygen, and with the partial reduction of vanadium pentoxide during its use as a catalyst for the oxidation of unsaturated hydrocarbons (*10–13*). Such observations suggest that the mechanism of oxidation over vanadium pentoxide of unsaturated fuels involves reduction of the catalyst by the fuel and its reoxidation by oxygen.

Little work has been reported on the

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oxidation over metal oxides of acyclic alkenes containing five or more carbon atoms. The present studies describe the vanadium-pentoxide–catalyzed oxidation of all five isomeric pentenes, in an attempt to discover the mechanism of formation of each type of product and to elucidate the role of the catalyst itself. The oxidation of branched-chain pentenes is considered here; similar work on straight-chain pentenes and studies of the properties of the catalyst itself will be described in subsequent papers.

Methods

(1) *Preparation and Purification of Pentenes*

(a) **2-Methylbut-2-ene.** 2-Methylbutan-2-ol was dehydrated with 33% (vol/vol) sulfuric acid, olefin being obtained in 84% yield. The redistilled olefin had a boiling point of 37°C and a refractive index (n_D^{20}) of 1.3868 (cf. literature b.p. of 2-methylbut-2-ene, 38.4°C and n_D^{20} 1.3874). The product was found to contain about 5% of 2-methylbut-1-ene (literature b.p., 31°C). These two isomers were separated gas-chromatographically (*14*). It was found, however, that under the conditions used during catalytic oxidation over vanadium pentoxide 2-methylbut-2-ene isomerizes rapidly to give about 20% of 2-methylbut-1-ene. In the preparation of fuel for catalytic studies, therefore, the separation of isomers is unnecessary and was carried out only on samples to be used in gas-phase studies.

(b) **2-Methylbut-1-ene.** 2-Methylbut-1-ene, obtained commercially, was treated with 5% aqueous sodium hydroxide to remove any sulfur dioxide, dried, and fractionally distilled. The purified olefin had b.p. 31.2°C and n_D^{20} 1.3780 (cf. literature, b.p. 31.05°C; n_D^{20} 1.3777) and was shown gas-chromatographically to contain less than 0.5% of other isomeric pentenes.

(c) **3-Methylbut-1-ene.** 3-Methylbut-1-ene, obtained commercially, was purified using methods similar to those described for 2-methylbut-1-ene, and had b.p. 20.7°C and n_D^{20} 1.3646 (cf. literature, b.p. 20.9°C; n_D^{20} 1.3643).

(2) *Preparation of the Catalyst*

The pumice-supported vanadium pentoxide catalyst was prepared by the method of Milas and Walsh (*15*). To a solution of 250 g of ammonium metavanadate (Analar) in 1000 ml of water was added 1000 g of 8–10 mesh (B.S.) pumice which had been heated previously at 200°C for 3 hr to remove adsorbed liquids and gases. The mixture was evaporated to dryness with continuous stirring, until the evolution of ammonia ceased. The temperature was not allowed to exceed 350°C. The impregnated support was then sieved to the required mesh size (8–10 mesh B.S.) using cloth sieves, since metal sieves (e.g., brass) introduced impurities, giving a catalyst of completely different activity. The solid thus obtained was heated in the reaction vessel at 350°C under vacuum for 4 hr to remove adsorbed ammonia and was then activated with oxygen at 350°C for 4 hr.

(3) *Catalytic Reactions: Apparatus and Procedure*

A gas-flow system was employed in which known mixtures of oxygen, nitrogen, and pentene were passed through a heated bed of catalyst and the emerging gas stream was analyzed. Oxygen and oxygen-free nitrogen from cylinders were purified from carbon dioxide and water vapor by passage through two purgers which consisted of 2 ft long cylindrical glass columns containing, respectively, Sofnolite (15% sodium hydroxide in calcium oxide) and Anhydrone (magnesium perchlorate) with silica gel as an indicator. The flow rates of the gases were regulated by sensitive needle valves and measured by capillary flow meters. One stream of nitrogen was diverted through a series of flasks containing liquid pentene. The first of these was maintained at a temperature (12°C) 2 C° higher than the other two and thus acted as a presaturator. In the third flask, the use of an immersed gas-jet bubbler and only a small liquid head reduced to a minimum the pressure drop across the saturator unit. A saturated, but not supersaturated, mix-

ture of fuel vapor at a known temperature in nitrogen was thus produced.

The separate gas streams (oxygen, nitrogen containing the organic vapor and auxiliary nitrogen) all entered a gas mixer, which consisted of a vertical glass column packed with glass spheres of a size such that the largest space between them was less than the quenching distance; the gas mixer thus acted as a flame trap also. The use of auxiliary nitrogen enabled the ratio of oxygen to pentene and the contact time to be varied independently without altering the flow rate of the fuel itself.

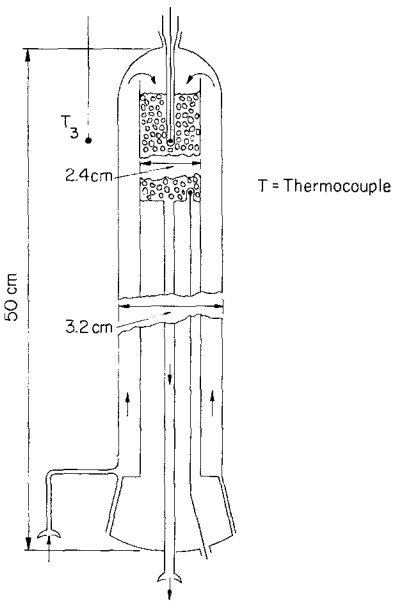


FIG. 1. Design of reactor.

The reactor (Fig. 1) was constructed of Pyrex glass and consisted of an outer jacket, 3.2-cm diam., and an inner tube, 2.4-cm diam., the upper end of which served as a container for the catalyst. The incoming gas mixture flowed up through the outer annulus, which acted as a heat exchanger, and down through the catalyst. The reactor was mounted vertically in an electrically heated tube furnace, the temperature of which was uniform over the length of the catalyst bed (9.6 cm) and was automatically controlled to within 0.2 C°. Chromel-alumel thermocouples measured the temperature of the catalyst itself (T_1), that of the gases leaving the catalyst (T_2), and that at a point in the furnace at the same height as the center of the catalyst (T_3).

The outlet tube of the reactor was of a volume small compared with that of the catalyst chamber, minimizing the extent of further reaction in the gas phase of oxidation products. The effluent gases were passed through a cold trap from which samples were withdrawn periodically for chemical analysis, or led via ice-cooled traps and a U-tube containing magnesium perchlorate to an infrared carbon dioxide analyzer. Samples for gas-liquid chromatographic analysis were collected in capillary U-tubes, maintained at —196°C, and fitted with a by-pass, situated between the reactor and the cold trap. With the reactor operating under steady conditions, the total effluent during a given time (usually 20 sec) was passed into the U-tube. Nitrogen and oxygen were removed by pumping and the remaining sample analyzed.

To prevent condensation of relatively involatile products, those parts of the apparatus beyond the reactor outlet were heated electrically to about 100°C.

This apparatus was used not only for studies of the vanadium-pentoxide–catalyzed reactions of pentenes, but also for the comparative work on the corresponding gas-phase reactions reported herein. Gas-phase reactions were investigated by replacing the catalyst with an equal volume of glass spheres of a similar mesh size.

(4) *Analytical Methods*

(a) Gas chromatography. C_1–C_{10} hydrocarbons and organic oxygenates were satisfactorily separated, identified, and estimated by using two columns. The first, on which analysis of oxygenates was effected, consisted simply of 12 ft of polyethylene glycol (M.W. 1500) (20% by weight) on alkali-washed 60–100 mesh Embacel, a specially treated form of kieselguhr, as solid support and was used at 81°C. The second, used for hydrocarbon analysis, employed two stationary phases in series; 19.5 ft of propylene carbonate

(27% by weight) and squalene (2.7% by weight) on 60–100 mesh acid-washed Embacel followed by 4.5 ft of silicone oil (M.S. 550) (30% by weight) on a similar support was used at 35.5°C. Peaks were identified by comparison of their retention volumes at several temperatures with those of known compounds and by addition of the latter to the oxidation products.

(b) **Infrared spectroscopy.** Carbon dioxide was estimated using an infrared gas analyzer (Type SC), calibrated directly by passing through it streams of air containing known amounts of carbon dioxide.

(c) **Chemical methods.** Peroxides were estimated iodometrically, the sample being kept under dry nitrogen (*16*). Formaldehyde was determined colorimetrically by the chromotropic acid method (*17*). Total acids were estimated by titration under nitrogen with 0.1 *N* aqueous sodium hydroxide using phenolphthalein as indicator.

Results

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

(a) **The effect of temperature.** The variation with temperature of product formation during the catalytic oxidation of 2-methylbut-2-ene is shown in Fig. 2. Even at temperatures as low as 220°C more than 20% of the fuel has isomerized to 2-methylbut-1-ene, but no oxygenated products are produced at temperatures below 240°C. At this temperature, acetaldehyde, acetone, 2,3-epoxy-2-methylbutane, 3-methylbutan-2-one, and C_{10} hydrocarbons are formed. Further increase of temperature causes a sharp decrease in the amounts of 2-methylbut-2-ene and 2-methylbut-1-ene, 50% of the former being consumed at 258°C, with concurrent increases in the amounts of oxygenated products, of which acetaldehyde and acetone are major. At temperatures above 270°C, appreciable quantities of ethylene and propylene are formed and these products are resistant to oxidation as the temperature is increased. Traces of butanone and *n*-butyraldehyde (not shown in Fig. 2) are also produced. No peroxides, formaldehyde, or unsaturated carbonyl compounds were detected under any conditions.

The effect of temperature on the gas-phase oxidation of 2-methylbut-2-ene, under conditions of reactant ratio and residence time similar to those used for catalytic reaction, was determined for comparative purposes (Table 1). The pattern of fuel consumption and of formation of acetaldehyde and acetone are similar in the gas phase and over the catalyst, the yields being somewhat higher in the former

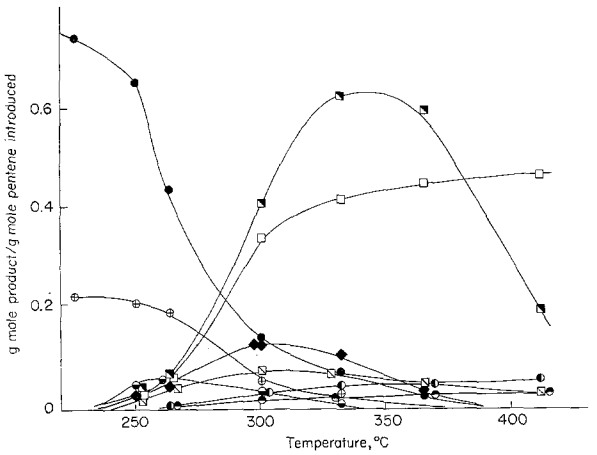


FIG. 2. The V_2O_5-catalyzed oxidation of 2-methylbut-2-ene: the effect of temperature. Contact time, 33.6 sec; oxygen/pentene = 1.25; ●, 2-methylbut-2-ene; ⊕, 2-methylbut-1-ene; ◥, acetaldehyde; □, acetone; ◹, 3-methylbutan-2-one; ◆, 2,3-epoxy-2-methylbutane; ◒, C_{10} hydrocarbons.

TABLE 1
THE OXIDATION OF 2-METHYLBUT-2-ENE: COMPARISON OF THE GAS-PHASE AND VANADIUM-PENTOXIDE–CATALYZED REACTIONS[a]

Product	Temperature (°C)	Yield (mole %, based on pentene introduced)	
		Gas-phase	V_2O_5-catalyzed
2-Methylbut-2-ene (remaining)	250°	69.5	65
	300°	12	14.5
	350°	1.5	4.5
	400°	1	0
2-Methylbut-1-ene	250°	13.5	21
	300°	6	6.5
	350°	1	1.5
	400°	0	0
Acetaldehyde	250°	9	3
	300°	85.5	40
	350°	22	62.5
	400°	2	30
Acetone	250°	9	2.5
	300°	53	32.5
	350°	90	43.5
	400°	91	46.5
3-Methylbutan-2-one	250°	1.5	2
	300°	9.5	7.5
	350°	24.5	6.0
	400°	27.5	3.5
2,3-Epoxy-2-methylbutane	250°	0	2.5
	300°	<1	13
	350°	<1	6.5
	400°	0	0
Butanone	250°	1.5	0
	300°	16.5	1
	350°	14	1
	400°	11.5	1
Methane	250°	0	0
	300°	1.5	0
	350°	14	0
	400°	20.5	0
Ethylene	250°	0	0
	300°	0	3
	350°	0	5
	400°	0	5.5
Propylene	250°	0	0
	300°	0	2
	350°	0	2.5
	400°	0	3

[a] Contact time 33.6 sec, oxygen:olefin = 1.25.

regime. In the gas phase, 50% of the fuel is consumed at 268°C, i.e., at a temperature only 10°C higher than the corresponding one for the catalytic reaction. The gas-phase reaction is less selective than the catalytic oxidation, considerable quantities of butanone and of methane but little 2,3-epoxy-2-methylbutane being formed. Small quantities of propionaldehyde, formaldehyde, and *n*-butyraldehyde are also formed.

(b) The effect of contact time. The effect of contact time on the products of oxidation of 2-methylbut-2-ene over vanadium pentoxide was studied both at 250°C, under which conditions only the primary products of reaction are formed, and at 300°C where the yields are much higher.

At 250°C, the consumption of 2-methylbut-2-ene increases sharply as the contact time is increased from 0 to 20 sec, being converted to 2-methylbut-1-ene and to smaller quantities of acetone, acetaldehyde, 2,3-epoxy-2-methylbutane, 3-methylbutan-2-one, and C_{10} hydrocarbons (Fig. 3). Trace quantities of ethylene and propylene are formed; no other products were detected. Further increase of contact time, however, causes only a small increase in fuel consumption, acetone and acetaldehyde being produced in increasing quantities. At contact times greater than 60 sec, the 2-methylbut-1-ene formed begins to be oxidized. (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 of this series.)

At 300°C, the variations with contact time of fuel consumption and of product formation are much more marked [Figs. 4(a) and (b)] than at 250°C. The organic products at low contact times include, in addition to acetaldehyde, acetone, 2,3-epoxy-2-methylbutane, 3-methylbutan-2-one, 2-methylbut-1-ene, and C_{10} hydrocarbons, considerable quantities of ethylene, propylene, butanone, and *n*-butyraldehyde. A large proportion of the fuel is converted to carbon dioxide. No peroxides or formaldehyde were detected.

(c) The effect of reactant ratio. The availability of gaseous oxygen was varied

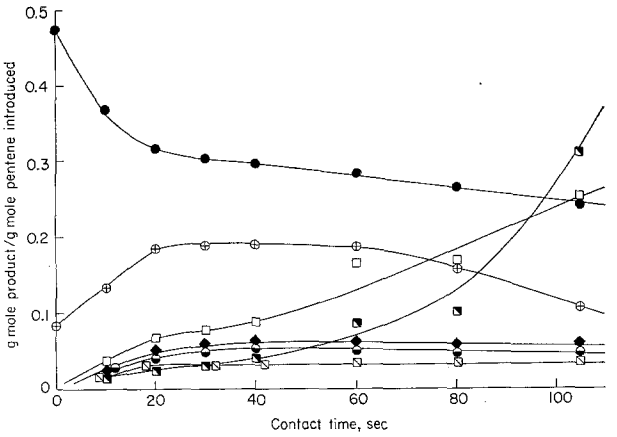


FIG. 3. The V_2O_5-catalyzed oxidation of 2-methylbut-2-ene at 250°C: the effect of contact time. Oxygen/pentene = 1.25; ●, 2-methylbut-2-ene; ⊕, 2-methylbut-1-ene; ◥, acetaldehyde; □, acetone; ◹, 3-methylbutan-2-one; ◆, 2,3-epoxy-2-methylbutane; ◒, C_{10} hydrocarbons.

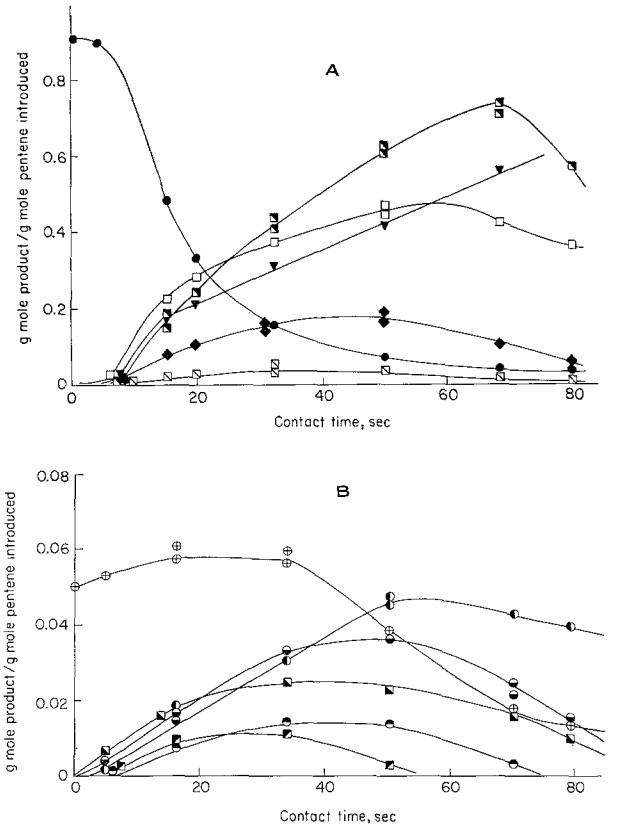


FIG. 4. The V_2O_5-catalyzed oxidation of 2-methylbut-2-ene at 300°C: the effect of contact time; A, major products; B, minor products; (oxygen/pentene = 1.25) (A) ●, 2-methylbut-2-ene; ◥, acetaldehyde; □, acetone; ▼, carbon dioxide; ◹, 3-methylbutan-2-one; ◆, 2,3-epoxy-2-methylbutane. (B) ⊕, 2-methylbut-1-ene; ◐, ethylene; ◒, C_{10} hydrocarbons; ◓, propylene; ◹, *n*-butyraldehyde; ◩, butanone.

from zero to three times the molar concentration of fuel and the effect on product formation at 250°C and at 300°C determined.

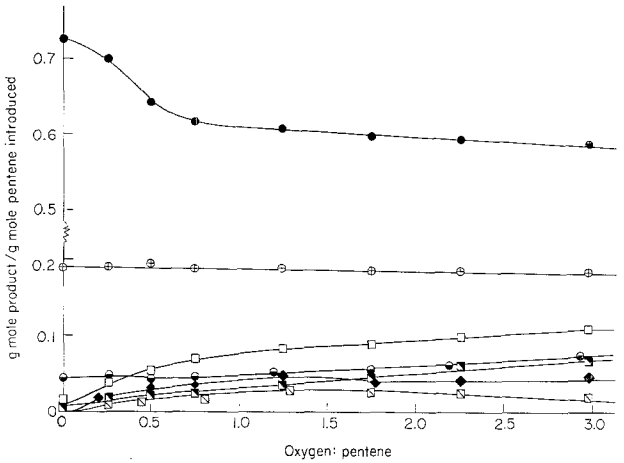


FIG. 5. The V_2O_5-catalyzed oxidation of 2-methylbut-2-ene at 250°C: the effect of reactant ratio; contact time, 33.6 sec.; ●, 2-methylbut-2-ene; ⊕, 2-methylbut-1-ene; ◒, C_{10} hydrocarbons; ◥, acetaldehyde; ◥, acetone; ◹, 3-methylbutan-2-one; ◆, 2,3-epoxy-2-methylbutane.

At 250°C (Fig. 5) in the absence of any gaseous supply of oxygen, 19 mole % of 2-methylbut-1-ene, 5 mole % of C_{10} hydrocarbons, and between 0.5 and 1 mole % of each of acetone and acetaldehyde are formed. The introduction of gaseous oxygen in increasing amounts causes a rise in fuel consumption and in the numbers and amounts of oxygenated products. Acetone and acetaldehyde are produced in gradually increasing amounts throughout the range of oxygen-to-pentene ratio 0 to 3, but the concentrations of 2,3-epoxy-2-methylbutane and 3-methylbutan-2-one reach shallow maxima at an oxygen-to-pentene ratio of about 1.25 and thereafter decrease.

At 300°C [Figs. 6(a) and (b)], 2-methylbut-1-ene, C_{10} hydrocarbons, acetone, and acetaldehyde are again formed in the absence of gaseous oxygen, under which conditions about 0.3% of ethylene and 0.2% of propylene are produced also. The introduction of oxygen causes the concentrations of remaining fuel, of 2-methylbut-1-ene, and of C_{10} hydrocarbons to decrease sharply, having an effect much more pronounced than that at 250°C, with concurrent increases in the formation of oxygenated products, ethylene, and propylene and the appearance of 2,3-epoxy-2-methylbutane, 3-methylbutan-2-one, butanone, *n*-butyraldehyde, and carbon dioxide. The organic oxygenated products and C_2 and C_3 alkenes reach maximum concentrations when the oxygen-to-pentene ratio is about 1.25 (with the exception of butanone, the maximum concentration of which is formed when the ratio is 0.8). Carbon dioxide, on the other hand, is produced in steadily increasing amounts as the availability of oxygen is increased.

(d) The carbon balance. Carbon balances for the heterogeneous catalytic oxidation of 2-methylbut-2-ene at 250°C and at 300°C are shown in Tables 2 and 3, respectively. In all cases the carbon input is accounted for, except under combinations of high temperature and high oxygen availability. Under these conditions the formation of large quantities of carbon oxides probably explains the discrepancy.

(2) The Oxidation of 2-Methylbut-1-ene

The products formed during the vanadium-pentoxide–catalyzed oxidation of 2-methylbut-1-ene are qualitatively similar to those formed under similar conditions from 2-methylbut-2-ene. The presence of a

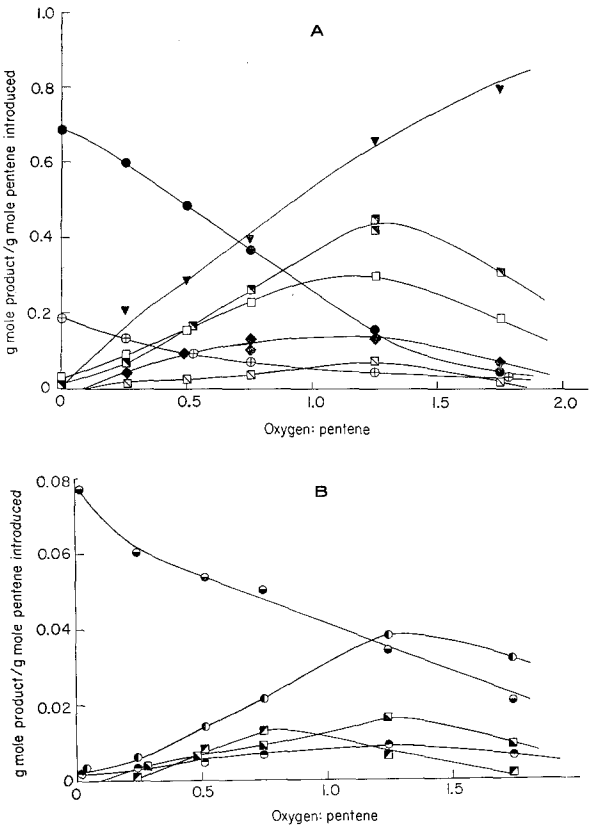


FIG. 6. The V_2O_5-catalyzed oxidation of 2-methylbut-2-ene at 300°C: the effect of reactant ratio; (A) major products; (B) minor products; contact time, 33.6 sec. (A) ●, 2-methylbut-2-ene; ⊕, 2-methylbut-1-ene; □, acetaldehyde; □, acetone; ◹, 3-methylbutan-2-one; ◆, 2,3-epoxy-2-methylbutane; ▼, carbon dioxide. (B) ◒, C_{10} hydrocarbons; ◐, ethylene; ◓, propylene; ◹, *n*-butyraldehyde; ◩, butanone.

TABLE 2

CARBON BALANCE: 2-METHYLBUT-2-ENE AT 250°C

Carbon input: 9.7 × 10^{-4} g. atoms/min Oxygen/olefin: Contact time (sec):	1.25 20	1.25 60	1.25 90	0.0 30	0.5 30	1.5 30	2.5 30
	Carbon output (% of carbon input)						
2-Me-but-2-ene	64.0	57.0	49.5	72.2	64.0	60.3	58.6
2-Me-but-1-ene	18.2	18.8	13.4	18.8	18.5	18.3	18.3
C_{10} hydrocarbons	8.0	10.6	9.2	9.0	9.0	9.0	9.0
Acetaldehyde	0.8	2.5	6.9	0.3	0.7	1.8	2.0
Acetone	3.8	6.9	11.8	0.3	3.8	4.5	6.3
2,3-Epoxy-2-methylbutane	5.0	5.3	5.6	—	2.4	3.3	5.6
3-Methylbutan-2-one	2.6	3.3	3.0	—	1.7	2.6	2.3
n-Butyraldehyde	—	0.4	0.5	—	—	—	—
Butanone	—	—	0.2	—	—	—	—
Total	102	105	100	101	100	100	102

TABLE 3
CARBON BALANCE: 2-METHYLBUT-2-ENE AT 300°C

Carbon input: 9.7 × 10^{-4} g. atoms/min Oxygen/olefin: Contact time (sec):	1.25 15	1.25[a] 33.6	1.25 60	0.0 33.6	0.25 33.6	0.75 33.6	1.25[a] 33.6	2.0 33.6
	Carbon output (% of carbon input)							
2-Me-but-2-ene	51.3	14.7	5.6	67	60	36	15.7	2.4
2-Me-but-1-ene	6.0	5.0	2.7	19	12.7	7.3	4.3	2.0
C_{10} hydrocarbons	6.7	6.6	6.0	16	13.3	9.2	6.7	2.0
Ethylene	0.7	1.2	1.8	0.1	0.23	0.8	1.5	1.3
Propylene	0.4	0.9	0.8	0.1	0.13	0.4	0.5	0.1
Acetaldehyde	7.0	17.4	28.0	0.2	2.7	10.2	17.3	7.5
Acetone	12.2	22.0	27.2	0.2	4.4	13.0	17.6	7.0
Carbon dioxide	3.4	6.5	10.0	—	1.5	4.1	6.3	9.1
2,3-Epoxy-2-methylbutane	7.3	16.0	14.0	—	6.8	12.7	13.3	3.7
3-Methylbutan-2-one	5.4	3.5	2.3	—	1.4	3.7	6.7	0.7
n-Butyraldehyde	0.3	0.9	1.7	—	0.3	0.6	1.9	0.5
Butanone	0.5	0.5	—	—	—	0.9	0.5	—
Total	101	95	100	103	103	99	92	37

[a] From two different series of runs.

large proportion of the latter hydrocarbon in the effluent gases and the subsequent pattern of oxidation suggest strongly that very extensive isomerization takes place on the catalyst. The amounts of products formed from 2-methylbut-1-ene and from 2-methylbut-2-ene at 300°C with an oxygen:pentene ratio of 1.25 and a contact time of 33.6 sec are compared in Table 4.

By contrast, the gas-phase oxidation of 2-methylbut-1-ene (Fig. 7) produces no

TABLE 4
A COMPARISON OF THE PRODUCTS OF THE VANADIUM-PENTOXIDE-CATALYZED OXIDATIONS OF THE THREE BRANCHED-CHAIN PENTENES[a]

Product	Yield (mole % based on fuel introduced) for the fuels: 2-Methyl-but-2-ene	2-Methyl-but-1-ene	3-Methyl-but-1-ene
2-Methylbut-2-ene	14.5	15.3	6.9
2-Methylbut-1-ene	6.5	7.0	0.5
3-Methylbut-1-ene	0	0	63.5
C_{10} hydrocarbons	3.5	10	1.8
Ethylene	3.0	2.5	Traces
Propylene	2.0	2.0	Traces
Acetaldehyde	40	37	2.7
Acetone	32.5	31	4.0
3-Methylbutan-2-one	7.5	Traces	0.3
Butanone	1.0	8.0	1.0
2,3-Epoxy-2-methylbutane	13	8.0	0.5

[a] Oxygen:pentene = 1.25; contact time, 33.6 sec; temperature, 300°C.

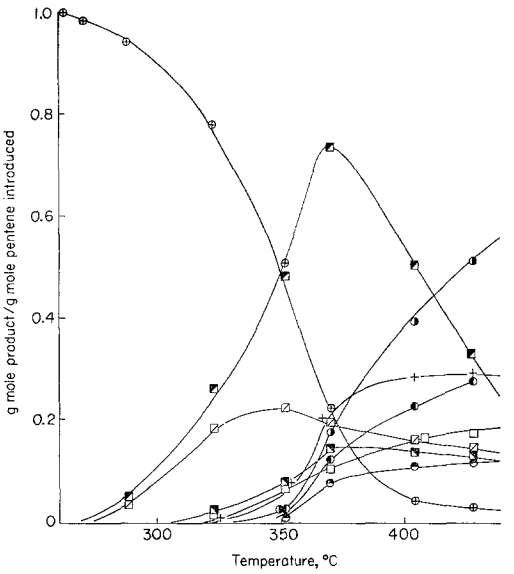


FIG. 7. The gas-phase oxidation of 2-methylbut-1-ene: the effect of temperature; residence time, 33.6 sec; oxygen/pentene = 1.25; ⊕, 2-methylbut-1-ene; ◩, butanone; ◰, formaldehyde; ◑, methane; ◐, ethylene; ◓, propylene; ◪, acetaldehyde; □, acetone; +, methanol.

2-methylbut-2-ene, and the major oxygenated products (butanone and formaldehyde) are markedly different from those derived from 2-methylbut-2-ene (acetone and acetaldehyde). Moreover, 2-methylbut-1-ene is much less reactive towards oxygen in the gas phase than is 2-methylbut-2-ene. Fifty per cent of the fuel is consumed at the relatively high temperature of 350°C, and butanone and formaldehyde are the only products below 320°C. At higher temperatures, methane, methanol, ethylene, acetaldehyde, acetone, and propylene are also formed.

(3) *The Oxidation of 3-Methylbut-1-ene*

The vanadium-pentoxide–catalyzed oxidation of 3-methylbut-1-ene again produces considerable quantities of 2-methylbut-2-ene and oxygenated products characteristic of the latter hydrocarbon (Table 4), although, under given conditions, the consumption of 3-methylbut-1-ene is far less than that of the other branched-chain pentenes.

In the gas phase, by contrast, 3-methylbut-1-ene produces no isomeric pentenes (Fig. 8) and its stability in the presence of oxygen, although higher than that of 2-methylbut-2-ene, is lower than that of 2-methylbut-1-ene, 50% of the 3-methylbut-1-ene being consumed at 305°C. The products of gaseous oxidation of 3-methylbut-1-ene are isobutyraldehyde, formaldehyde, propylene, acetaldehyde, and ethylene.

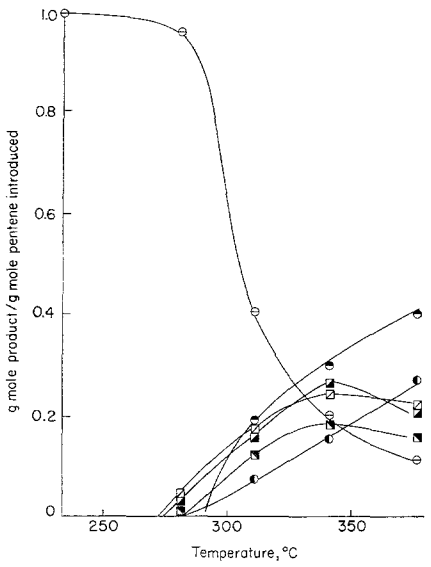


FIG. 8. The gas-phase oxidation of 3-methylbut-1-ene: the effect of temperature; residence time, 33.6 sec; oxygen/pentene = 1.25; ⊖, 3-methylbut-1-ene; ◓, propylene; ◪, isobutyraldehyde; ◥, acetaldehyde; ◐, ethylene; ◰, formaldehyde.

(4) *The Isomerization of Branched-Chain Pentenes on Vanadium Pentoxide*

The occurrence of extensive isomerization and dimerization during the oxidation of branched-chain pentenes over vanadium pentoxide was investigated further by studying the isomerization of each pentene in the absence of oxygen, both on the catalyst and in the gas phase. The results at 300°C with a contact time of 33 sec are shown in Table 5. Over vanadium pentoxide, about 20% of 2-methylbut-1-ene and 13% of C_{10} hydrocarbons are formed from 2-

TABLE 5
THE ISOMERIZATION OF BRANCHED-CHAIN PENTENES[a]

Products	Pentene introduced: 2-Methylbut-2-ene	2-Methylbut-1-ene	3-Methylbut-1-ene
(a) *Over pumice-supported vanadium pentoxide*			
Pent-1-ene	—	0.1	—
Pent-2-ene (*trans*)	—	0.1	—
Pent-2-ene (*cis*)	0.8	0.1	—
2-Methylbut-1-ene	19.6	57.3	1.8
3-Methylbut-1-ene	—	0.3	91.2
2-Methylbut-2-ene	66.5	40.3	4.1
C_{10} hydrocarbons	13.3	2.4	2.9
Total	100.2	100.3	100.0
(b) *In the gas phase*			
Pent-1-ene	—	0.2	—
Pent-2-ene (*trans*)	0.1	—	—
Pent-2-ene (*cis*)	0.2	—	—
2-Methylbut-1-ene	1.0	99.4	—
3-Methylbut-1-ene	0.6	0.4	100.0
2-Methylbut-2-ene	98.0	—	—
C_{10} hydrocarbons	0.2	—	—
Total	100.0	100.0	100.0

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

methylbut-2-ene. As much as 40% of 2-methylbut-2-ene is formed from 2-methylbut-1-ene, which also gives small quantities of all the other pentenes. 3-Methylbut-1-ene is isomerized comparatively little, producing only 4.1% of 2-methylbut-2-ene and 4.7% of other products. In the gas phase, the extent of isomerization is far lower. Only 2.0% of 2-methylbut-2-ene, and 0.6% of 2-methylbut-1-ene isomerize, whereas 3-methylbut-1-ene is completely unchanged.

Discussion

The main products formed during the heterogeneous catalytic oxidation of 2-methylbut-2-ene over pumice-supported vanadium pentoxide are acetaldehyde, acetone, 3-methylbutan-2-one, 2,3-epoxy-2-methylbutane, propylene, and ethylene. These products are characteristic of the addition of oxygen at the double bond of the pentene and, in the case of carbonyl and olefinic scission products, subsequent rupture at the position of the double bond. Over vanadium pentoxide, the oxidations of the other branched-chain pentenes give the same products as does that of 2-methylbut-2-ene, in contrast to the gaseous oxidations of these compounds. It is evident that isomerization of terminal olefins is occurring on the catalyst, producing 2-methylbut-2-ene, and that this isomer is subsequently oxidized. The production of 2-methylbut-2-ene in substantial quantities by oxidation of 2-methylbut-1-ene and of 3-methylbut-1-ene (Table 4) and the extensive isomerization of branched-chain pentenes on the catalyst (Table 5) strongly support this conclusion. Of these three pentenes, 2-methylbut-2-ene is the most reactive towards oxygen in the gas phase and is oxidized over vanadium pentoxide as readily as 2-methylbut-1-ene and more readily than 3-methylbut-1-ene. It is established, then, that the vanadium-pentoxide–catalyzed oxidation of all three branched-chain pentenes is described by their isomerization to 2-methylbut-2-ene and the ready oxidation of this pentene. The mechanism operative in the case of this fuel, therefore, is a general one for branched-chain pentenes.

Although the major carbonyl compounds and the epoxide formed during the V_2O_5-catalyzed oxidation of 2-methylbut-2-ene are similar to the major products of the gas-phase oxidation, there are significant quantitative differences. In particular, over vanadium pentoxide the concentrations of acetone and acetaldehyde produced are not equimolar, even at low contact times and low temperatures (Fig. 3), in marked contrast to the gas-phase reaction (*14*). Again, the concentrations of 2,3-epoxy-2-methylbutane formed over vanadium pentoxide are far higher than those in the gas phase, while those of 3-methylbutan-2-one are considerably lower. In addition, no peroxides are produced over vanadium pentoxide. It seems unlikely therefore that the mechanism of the heterogeneous oxidation resembles closely that of gas-phase oxidation (*14, 18*); attack by gaseous molecular oxygen of the olefin probably plays only a minor role, in contrast to the suggested mechanism for the vanadium-pentoxide–catalyzed oxidation of butenes in which gaseous molecular oxygen is the active oxidant (*9*).

As the velocities of the catalyzed and gas-phase oxidations are not markedly different, however, the possible contribution to the former process of homogeneous reaction should be considered. It has been shown (*19*) that, during the oxidation of propylene over a catalyst consisting of bismuth, phosphorus, and molybdenum oxides, 1,2-epoxypropane is formed solely in the post-catalyst zone, its formation being initiated by aldehydes formed during heterogeneous reaction. In the present studies, this zone has a volume small compared with that of the catalyst-filled reactor (Fig. 1). It is conceivable, however, that reaction occurs in the larger precatalyst zone, although there are, of course, no aldehydes present there. If 2,3-epoxy-2-methylbutane were indeed formed in the precatalyst zone, the absence of the epoxide from the products of gas-phase reaction would necessitate its complete conversion to 3-methylbutan-2-one at the surface of the glass

spheres used in these studies. Moreover, at 250–300°C in an empty reactor, gaseous oxidation of 2-methylbut-2-ene should produce considerable amounts of 2,3-epoxy-2-methylbutane. This is not so; not only is the epoxide absent but 3-methylbutan-2-one, a major product, is not formed via the epoxide (*14*). The absence of methane from the products of the V_2O_5-catalyzed oxidation at temperatures greater than 350°C, despite its formation in large quantities during gas-phase reaction under similar conditions (Table 1) is further evidence that, in the presence of the catalyst, the contribution of homogeneous steps is small. It is likely, therefore, that the oxidations reported in the present studies are predominantly heterogeneous. This conclusion is strongly supported by the occurrence, in addition to isomerization and dimerization, of true oxidation of pentenes on the catalyst in the absence of any gaseous supply of oxygen. The fuel reacts with the oxygen of the catalyst itself to form small quantities of acetone, acetaldehyde, and lower olefins; under these conditions, it is evident that the oxygen incorporated in the gaseous products was originally present in the form O^{2-}. It is most probable therefore that, even in the presence of gaseous oxygen, these products are formed by the reaction of adsorbed olefin species with O^{2-}.

The adsorption on vanadium pentoxide due to donation of an electron from the π bond of the olefin, with resultant opening of the bond, will produce two kinds of surface-bonded cations

$$(CH_3)_2C{=}CHCH_3 \rightarrow (CH_3)_2\overset{+}{C}{-}CHCH_3 \quad \text{and}$$

(I)

$$(CH_3)_2C{-}\overset{+}{C}HCH_3$$

(II)

The interaction of O^{2-} with (I) and (II) will give, respectively, the surface-bonded anions

$$(CH_3)_2\overset{O^-}{C}{-}CHCH_3 \quad \text{and} \quad (CH_3)_2\overset{O^-}{C}{-}CHCH_3$$

(III) (IV)

Scission of the central C–C bond of these anions will give carbonyl scission products and the remaining surface-bonded carbanions can readily rearrange, by electron transfer to the surface and H shift, to olefinic scission products. Thus the breakdown of (III) gives acetone and ethylene, and similar reaction of (IV) gives acetaldehyde and propylene

$$(CH_3)_2\overset{O^-}{C}{-}CHCH_3 \rightarrow (CH_3)_2C{=}O + {}^-CHCH_3$$

(III) (V)

$$\rightarrow CH_2{=}CH_2$$

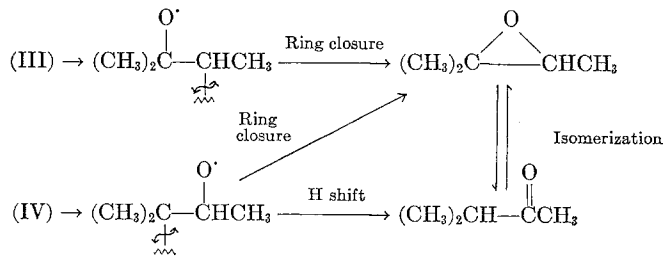
$$(CH_3)_2\overset{O^-}{C}{-}CHCH_3 \rightarrow CH_3CHO + CH_3\overset{-}{C}CH_3$$

(IV) (VI)

$$\rightarrow CH_3CH{=}CH_2$$

It seems likely that this is the major route by which the interaction of adsorbed olefin with the predominant oxygen species present leads to products. Acetone and acetaldehyde are, however, produced in larger quantities than ethylene and propylene, probably due to the further oxidation (to acetaldehyde and acetone, respectively) of (V) and (VI). The production of non-equivalent amounts of acetone and acetaldehyde indicates that the adsorption of the olefin does not lead to equal amounts of the cations (I) and (II).

If the adsorbed anions (III) and (IV) lose an electron to the surface before the C–C bond breaks, the resulting adsorbed alkoxy radicals may rearrange to give 2,3-epoxy-2-methylbutane and 3-methylbutan-2-one. The reactions with O^{2-} of adsorbed olefin are therefore capable of explaining in principle the six major organic products of the oxidation of 2-methylbut-2-ene. The small quantities of butanone formed probably arise by isomerization of 2-methylbut-2-ene to 2-methylbut-1-ene on the surface followed by oxidation of the surface cations characteristic of this species. The occurrence of isomerization and of dimerization of pentenes and the independence of oxygen



availability at low temperatures of the amounts of isomers and dimers formed suggests that adsorbed pentenes can lose hydrogen to the surface reversibly; π-allylic complexes are probably formed in a way analogous to that on transition metals (*4*).

The function of gaseous oxygen is probably merely that of regenerating the O^{2-} of the catalyst itself, in agreement with the mechanism of oxidation over vanadium pentoxide of unsaturated fuels postulated by Mars and van Krevelen (*10*). The overall mechanism of oxidation of branched-chain pentenes may therefore be summarized:

$$RH \xrightarrow{V^{5+}} RH^{+}_{(ads)} + \epsilon$$

$$RH^{+}_{(ads)} + O^{2-}_{(ads)} \rightarrow \text{products} + \epsilon$$

$$\tfrac{1}{2}O_{2(g)} + 2\epsilon \rightarrow O^{2-}_{(ads)}$$

If, as seems likely (*10–13*), the last of these steps is rate-determining, the catalyst will gradually be reduced and on an "old" catalyst (i.e., one which has been reduced) reactions of the adsorbed fuel with the intermediate oxygen ions O^- and O_2^- and indeed with molecular oxygen itself may become important. Reactions with adsorbed fuel of O^- analogous to those of O^{2-} give surface-bonded alkoxy radicals and eventually 3-methylbutan-2-one and 2,3-epoxy-2-methylbutane; those of O_2^- or O_2 give surface-bonded alkylperoxy radicals which will either decompose to give equimolar quantities of acetone and acetaldehyde or will participate in hydroperoxylation. The resulting mechanism will then resemble that of low-temperature gaseous oxidation, but it appears that under the present conditions this stage has not been reached.

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