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Dehydrodimerization of Propylene Using Bismuth Oxide as the Oxidant

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Bismuth oxide, Bi_2O_3, serves as an oxidant for the conversion of propylene to mainly 1,5-hexadiene. The main secondary product is benzene with small amounts of normal and cyclohexadiene also formed. The formation of 1,5-hexadiene most likely involves the combination of two allylic radicals. As the reaction temperature is increased from 475 to 500°C, the yield of 1,5-hexadiene decreases while the benzene yield increases. To selectively produce 1,5-hexadiene from propylene, the reaction has to be carried out cyclically, where the propylene reacts with bismuth oxide for a given period of time, and then the oxygen that is consumed is rapidly replenished with air. If a sufficient amount of gas-phase oxygen is used with propylene, the bismuth oxide serves as a catalyst to give a continuous reaction.

INTRODUCTION

The use of metal oxides as oxidants for hydrocarbons has been recognized for some time. It has been reported that butenes can react directly with Fe_2O_3 to form butadiene, water, and Fe_3O_4 (*1*). When propylene is passed over selenium dioxide at 300–330°C, it is converted to acrolein and water (*2*). The selenium dioxide is reduced to elemental selenium. Oxides of arsenic, antimony, and bismuth have been used as oxidants to convert isobutyraldehyde to methacrolein, water, and lower valence oxides (*3*). It has been claimed that propylene can be converted to propylene oxide using thallic oxide as the oxidant (*4*). Recently, it has been reported that 1,5-hexadiene can be prepared by contacting propylene with lead, cadmium, thallium (*5, 7*), and manganese oxides (*8*) at high temperatures. This prompts us to report our results on the dehydrodimerization of propylene to form mainly 1,5-hexadiene using bismuth oxide, Bi_2O_3, as the oxidant. The selective preparation of 1,5-hexadiene from only propylene is a considerable improvement over previous methods reported. Other methods require the use of hydrogen peroxide or other expensive starting materials (*9–14*).

EXPERIMENTAL

Preparation of Unsupported Bi_2O_3

The bismuth oxide used as the oxidant and catalyst was prepared by dissolving $Bi(NO_3)_3 \cdot 5H_2O$ (Fisher reagent grade) in dilute nitric acid ($6\,N$) and adding distilled water until the white hydrated bismuth oxide ceased to form. The precipitate was washed several times with distilled water, filtered, oven dried at 120°C for 16 hr, calcined for 24 hr at 600°C, and then broken into 10–20 mesh particles. The surface area of the bismuth oxide after such a treatment was 1.5 m^2/g as determined by the BET method using a krypton adsorbate. Examination of the bismuth oxide by X-ray diffraction revealed that the light yellow powder was α–Bi_2O_3. X-Ray diffraction patterns were obtained with a Norelco diffractionator, using nickel-filtered Cu K_α radiation. The impurities in the Bi_2O_3 were determined by a spectrographic

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ash analysis. The results showed that aluminum and sodium were present in the range of 0.01–0.1%, and calcium, silicon, and titanium were present in amounts less than 0.01%.

Preparation of Supported Bi_2O_3

Supported Bi_2O_3 was prepared by dissolving the calculated amount of $Bi(NO_3)_3 \cdot 5H_2O$ in a minimum of concentrated nitric acid, stirring in 100 g of support, and evaporating the mixture to dryness on a hot plate. Any Bi_2O_3 which did not adhere to the support was redissolved in a small amount of nitric acid, poured over the support, and again evaporated to dryness. The catalyst was then calcined in air at 550°C overnight. The weight percentage of Bi_2O_3 was determined by the weight gain of a given volume of catalyst and checked by a gravimetric bismuth analysis. The main support or carrier used was a low surface-area alumina, 0.1 m^2/g, in 3–5 mesh granular form, obtained from the Carborundum Company, designated as type AMM. This designation means that it is a fused aluminum oxide, with medium porosity (40–50%) and with medium pore composition (the average pore size in the 0.03 to 88 μ range is 39).

Reagents

Matheson CP grade propylene was used in all experiments. Calibration samples of 1,5-hexadiene, 2,4-hexadiene, 1,4-hexadiene, 1,3-cyclohexadiene, and 1,4-cyclohexadiene were obtained from the Aldrich Chemical Company, Inc. 1,3-Hexadiene was obtained from the K & K Chemical Company. The structures of these samples were verified by infrared and NMR. Acrolein and benzene were obtained from the Fisher Scientific Company.

Reactor

The reactor consisted of a 1-in. o.d. quartz tube, 15 in. long, with a concentric thermowell. An amount of oxidant (usually 25 cm^3) sufficient to form a bed 3 in. in length was added to the reactor. Silicon carbide was added above and below the catalyst bed to make a total solids zone 6–8 in. in length. Heating was accomplished by means of a cylindrical electric furnace, 9 in. long and 3 in. in diameter, connected to a variac and controlled by a Foxboro potentiometer (Model 4036). The furnace was positioned so that the catalyst was centered within it. The reactor was attached to the feed line by means of a ground glass joint having a ¼ in. glass-to-metal Kovar seal. Helium, air, and the propylene-nitrogen feed mixture were metered through calibrated micrometer valves (Nuclear Products Company, Cleveland, Ohio). The preset flows were controlled by solenoid valves (Skinner Electric Valves, No. V5D26510, ⅛ in. orifice) wired to a Synchron cycle timer. The oxidant was heated to the desired reaction temperature in air. This was followed by a 2½ min helium flush, a 10-min reaction cycle, a 2½ min helium flush, and a 10-min air-regeneration cycle. This sequence was repeated as long as necessary either automatically or manually. Temperatures within the catalyst or oxidant bed were monitored by means of multiple thermocouples positioned at ½-in. intervals along the length of the bed. In all of the experiments using Bi_2O_3 as the oxidant, the temperature variation across the Bi_2O_3 was only ±3°C. Space time variations were made by changing the propylene throughput at a constant propylene partial pressure with a fixed amount of Bi_2O_3. Figure 1 shows a schematic diagram of the reactor system.

Analytical

The gaseous effluent from the reactor was analyzed by gas-solid chromatography at various intervals during the 10-min reaction cycle. A Varian-Aerograph (Series 1800) chromatograph was used with a 20 ft × ¼ in. stainless steel column packed with Dow-Corning 200 on 60/80 mesh acid-washed Chromosorb P. Sampling was accomplished either manually by withdrawing a sample of the effluent with a gas hypodermic syringe, or semiautomatically by means of a solenoid-operated Varian Aerograph 2-position, 6-port linear gas sampling valve (V-A Part No. 57-000065-00). The

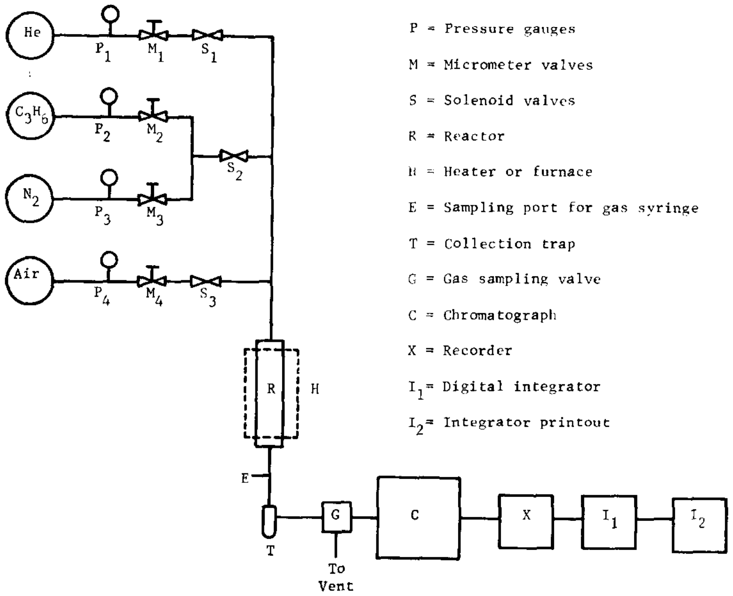


FIG. 1. Scheme of apparatus used.

gas syringe had to be used when sampling was made after a short reaction time, because there was not enough time to sufficiently flush out the gas sampling valve. The column oven was maintained initially at 50°C in order to obtain separation of the N_2 and CO_2 peaks. When these were eluted, the temperature was rapidly increased to 180°C and left there until the rest of the peaks were eluted. The peak areas were obtained with a Varian-Aerograph Model 480 electronic-digital integrator in conjunction with a Victor Digitmatic printer.

RESULTS

Unsupported Bismuth Oxide

Contacting propylene with Bi_2O_3 at high temperatures initially results in a very exothermic reaction with the formation of mainly carbon dioxide. If the Bi_2O_3 is treated long enough, it reduces to bismuth metal. However, if a short reaction time is used followed by air treatment to replenish the oxygen consumed, there is a dramatic change in product selectivity. Table 1 gives data on the reaction of Bi_2O_3 with propylene for reaction times of 10 min followed by a 10-min air treatment. The air treatment consisted of passing air over the reduced Bi_2O_3 at the same temperature and space velocity as the propylene. The values reported in Table 1 were taken at 4 min of the reaction cycle. For the first cycle, propylene was reacted with Bi_2O_3 at 475°C, and during the reaction, the temperature across the bed rose approximately 100°C. The main product formed was carbon dioxide. This is consistent with reports that Bi_2O_3 is inactive or gives only combustion products. For the second cycle there was a dramatic change in products with the selectivity to carbon dioxide decreasing and the initiation of 1,5-hexadiene formation. As the number of cycles increased, the conversion declined and approached a constant value; the selectivity to benzene and carbon dioxide decreased, and the selectivity to 1,5-hexadiene increased. The temperature was then increased to a value greater than the highest temperature to be studied for a given set of experiments. The reduction-oxidation cycles were continued until a constant-conversion value was attained. At this stage the Bi_2O_3 is considered "lined-out." This change in activity is mainly due

TABLE 1
LINING-OUT UNSUPPORTED BISMUTH OXIDE

Temp. °C	Cycle No.	Conversion (mole %)	Selectivity (Mole %)									
			CO_2	Acrolein	2,4-Hexadiene	1,5-Hexadiene	1,3-Hexadiene	1,4-Hexadiene	Benzene	1,3-Cyclohexadiene	1,4-Cyclohexadiene	*UK*
475	1	78.21	63.5	0.3	—	1.0	—	—	35.2	—	—	0.3
475	2	28.24	25.8	1.0	0.3	26.0	2.0	1.9	42.1	0.8	—	—
475	3	23.79	23.2	1.0	0.3	34.3	—	1.1	34.8	2.9	0.3	—
475	4	20.86	20.0	1.0	0.4	41.2	2.1	1.2	30.9	3.1	—	—
560	5	51.70	27.2	3.9	0.9	16.2	0.9	0.3	47.2	1.9	0.8	0.7
560	6	41.95	22.1	3.8	1.2	24.2	1.6	0.5	42.5	2.3	0.9	0.8
560	7	36.43	20.5	3.9	1.5	28.5	1.6	0.6	37.8	3.3	1.5	0.9
560	9	32.14	18.4	3.9	1.5	31.8	4.0	2.5	32.5	3.8	0.7	1.0
560	10	28.72	18.0	4.0	1.9	35.1	2.1	0.8	30.5	3.5	0.3	0.6
560	11	28.00										

Propylene GHSV = 190

UK = Unknown

TABLE 2

PROPYLENE CONVERSION AND PRODUCT SELECTIVITY VALUES AT VARIOUS TIMES IN THE REACTION CYCLE USING UNSUPPORTED Bi_2O_3 AT 520°C AND GHSV OF 190

		Selectivity (Mole %)								
Time (min)	Conversion (mole %)	CO_2	Acrolein	2,4-Hexadiene	1,5-Hexadiene	1,3-Hexadiene	1,4-Hexadiene	Benzene	1,3-Cyclohexadiene	1,4-Cyclohexadiene
1	17.17	15.3	2.4	1.5	54.6	1.5	0.5	19.9	3.3	1.0
4	17.50	12.6	2.3	1.3	57.9	1.3	0.5	19.7	3.8	0.5
8	17.50	11.4	2.1	1.3	56.1	2.3	0.8	20.7	4.1	1.3
130	11.59	8.3	1.2	0.7	67.2	3.9	0.7	14.2	3.2	0.6
180	10.31	7.4	1.7	0.6	71.2	4.3	0.5	11.4	2.4	0.5
240	8.96	7.1	1.6	0.6	71.4	4.5	0.1	10.8	3.5	0.4
300	8.43	6.3	1.3	0.6	72.1	4.6	0.6	8.7	4.3	1.5
450	6.70	6.3	1.3	0.7	76.0	5.5	0.4	6.1	3.6	—
Sample treated with air for 1 hr at 520°C										
4	12.06	9.1	2.2	1.7	62.9	2.8	0.7	13.8	5.1	1.8
Sample treated with air for 16 hr at 520°C										
4	15.58	11.7	2.4	2.2	58.5	2.1	0.8	17.1	3.7	1.5

to the loss of Bi_2O_3 surface area during the reduction-oxidation cycles. Initially the surface area was 1.5 m^2/g and this declined to 0.2 m^2/g for the "lined-out" Bi_2O_3.

Table 2 gives data for the variation of the propylene conversion and selectivity over a period of time using the "lined-out" Bi_2O_3. These data show that the conversion and selectivity remain fairly constant during the 10-min reaction period. Also included in this table are data showing the conversion and selectivity for continued Bi_2O_3 reduction without any regeneration. These data show that the reaction cycle can be fairly long. It is interesting to note the change in selectivity with time. Initially, less 1,5-hexadiene and more benzene and carbon dioxide are formed as compared to the respective amounts formed after a considerable amount of the Bi_2O_3 had been reduced. The increase in selectivity to benzene and carbon dioxide is most likely due to the high-initial oxygen concentration, and as the oxygen concentration declines, the tendency for 1,5-hexadiene to go on to benzene declines as does the formation of carbon dioxide from any hydrocarbon source.

The Bi_2O_3 can be reacted with propylene for 1 hr at 520°C and a GHSV of 190 and then regenerated back to its original activity by treating with air for 1 hr. Longer reduction times result in overreduction where the Bi_2O_3 cannot be restored to its original activity. For example, reduction of Bi_2O_3 for 7 hr (70% of the oxygen consumed) followed by 1 hr air regeneration only resulted in 69% of the original activity. Prolonged air treatment (16 hr) resulted in additional conversion but not a restoration of the original activity (see Table 2). Examination of a sample of the Bi_2O_3 that had been reacted with propylene for 10 min by X-ray showed only diffraction lines due to α-Bi_2O_3. A sample of Bi_2O_3 which had been reacted with propylene for 1 hr exhibited X-ray diffraction lines due to α-Bi_2O_3 and bismuth metal. After treating this sample with air for 1 hr, only lines attributable to α-Bi_2O_3 were observed. Bi_2O_3 which had been treated with propylene for a long time, i.e., 16 hr, and could not be restored to its original activity exhibited lines due to bismuth metal even after prolonged treatment with air. No other X-ray diffraction lines besides α-Bi_2O_3 and bismuth metal were observed at any time. Also, no reference could be found on the existence of BiO or Bi_2O species. Thus, the reduction of Bi_2O_3 with propylene most likely involves the conversion of Bi^{3+} directly to metallic bismuth. If the reduction is not taken too far, the bismuth metal must be dispersed as small crystallites in a Bi_2O_3 matrix which are capable of fairly rapid reoxidation back to Bi_2O_3. However, if the reduction is taken too far, there is coalescence of the bismuth metal to form large crystallites or a film which is difficult to oxidize back to Bi_2O_3. Coalescence would be expected since bismuth is liquid above 271°C. It should also be mentioned that the entire 10-min air treatment is not necessary to replenish the oxygen consumed from the Bi_2O_3 after a 10-min reaction period. This reoxidation is very rapid; however, a 10-min period was used to assure complete reoxidation.

In all the experiments, the propylene partial pressure was 0.67 atm with nitrogen as a diluent. The nitrogen also served as an internal standard to determine the propylene conversion. Figures 2 and 3 show the variation of the selectivity to products as a function of temperature and space time, respectively. Higher temperatures and increased space times resulted in a decrease in selectivity to 1,5-hexadiene and increased selectivity to benzene and carbon dioxide. The selectivity to the hexadiene and cyclohexadiene isomers did not vary much. These results show that 1.5-hexadiene isomerizes, cyclizes, and then dehydrogenates to benzene as temperature and space time are increased.

Figure 4 shows a plot of $-\ln C/Co$ as a function of time, where C is the concentration of propylene at any time, and Co is the original concentration. These plots give reasonably good straight lines through the origin, indicating an overall first-order conversion of propylene. This agreement

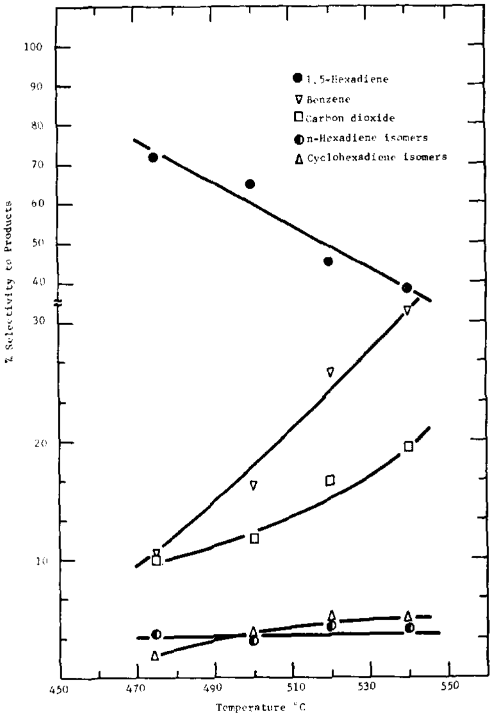


Fig. 2. Variation of product selectivities with temperature using unsupported Bi_2O_3 at a propylene GHSV of 190.

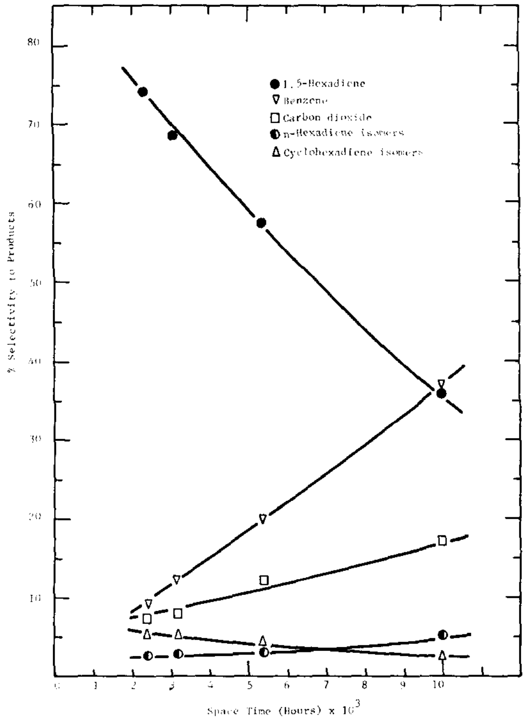


Fig. 3. Variation of product selectivities with space time using unsupported Bi_2O_3 at 520°C.

suggests that there are two irreversible first-order propylene reactions in parallel where propylene goes to 1,5-hexadiene and to carbon dioxide. It is realized that this is a gross oversimplification of the kinetics since 1,5-hexadiene isomerizes and dehydrocyclizes, and any one of these C_6 products can go to carbon dioxide. The variation of the observed rate constants with temperature obeys an Arrhenius relationship, as shown in Fig. 5, giving an apparent activation energy of 27.5 kcal/mole. The amount of bismuth oxide consumed during the reaction cycle is quite low. At 520°C, GHSV of 190, only about 5% of the Bi_2O_3 is consumed after 10 min. Because of this the concentration of surface oxygen is considered essentially constant, and a surface-dependency term is ignored in determining the rate constants.

Supported Bismuth Oxide

The use of bulk Bi_2O_3 granules or ¼-in. pellets of approximately 15-lb crush strength was not entirely satisfactory for long-term cyclic operation. After about one week of continuous cyclic operation, there was physical attrition of the Bi_2O_3 pellets or granules to fines, and in several places the pellets were fused to one another. This attrition is due to the surface contraction and expansion which the bismuth undergoes during the reaction-oxidation cycles. To minimize this problem Bi_2O_3 was supported on various carriers and tested. High surface-area supports gave unsatisfactory performance because of poor selectivity. An oxidant consisting of 21 wt % Bi_2O_3 on alumina (0.1 m^2/g) exhibited good activity and stability. This oxidant was used for 336 hr of continuous operation and an additional 200 hr without loss of activity or attrition. This percentage of Bi_2O_3, i.e., 21%, was found to be the maximum amount that could be supported on this alumina; additional Bi_2O_3 flaked off. The supported material was different than the unsupported Bi_2O_3 in that a higher temperature had to be used in order

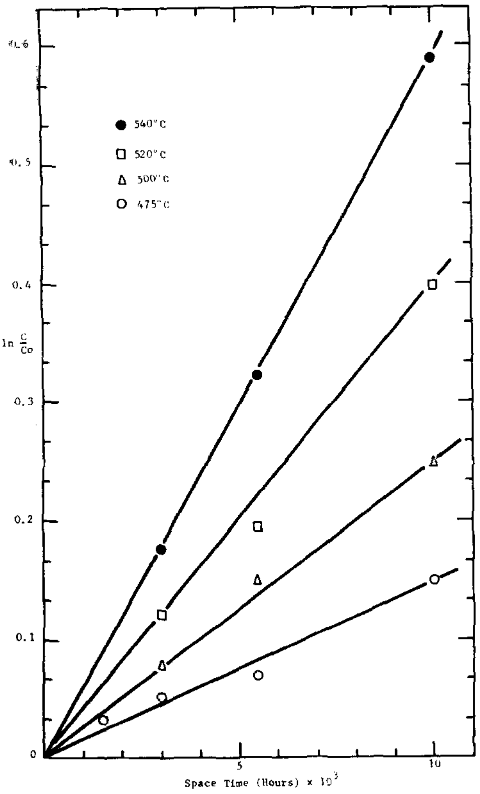


FIG. 4. First order plots using unsupported Bi_2O_3.

to obtain a comparable level of activity as the unsupported Bi_2O_3. Also, there was a fairly rapid decline in conversion during the reaction; whereas, with the unsupported Bi_2O_3 the conversion was nearly constant for the 10-min reaction time. Table 3 gives data showing the decline in conversion and selectivity changes during the reaction cycle. After 20 min of reaction without intermittent air treatment, the conversion had declined approximately 70% from the original activity. The data used in the following plots were taken after 4 min of the reaction cycle. The conversion at this time closely approximated the average propylene conversion for the entire 10-min reaction period.

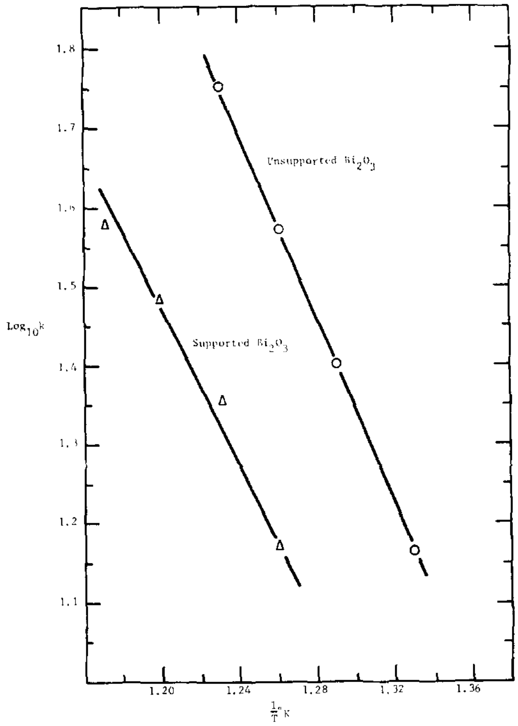


FIG. 5. Variation of reaction rates with temperature.

Figures 6 and 7 show the variation of the selectivity to products as a function of temperature and space time, respectively, for supported Bi_2O_3. The same trends in relative product selectivities were found as with the unsupported Bi_2O_3. The slight differences noted between the selectivities between the supported and unsupported Bi_2O_3 are due to the different temperature ranges studied. Figure 8 shows the first-order plots for the conversion of propylene over the temperature range 520 to 580°C. The space times used for these plots were based on the entire bed volume, i.e., Bi_2O_3 plus Al_2O_3. At a given temperature, the reaction rate constant for the supported Bi_2O_3 is about half that obtained with the unsupported Bi_2O_3. However, the reaction rate constant for the supported Bi_2O_3 is more than double that obtained with the unsupported Bi_2O_3 based on the absolute amount of Bi_2O_3 involved. With the supported Bi_2O_3, more of the available oxygen is consumed over a cycle period. For example, after 10 min at 560°C and a propylene GHSV of 190, approximately 30% of the available oxygen is consumed. An Arrhenius plot of these rate data is shown in Fig. 5, giving an apparent activation energy of 21.5 kcal/mole.

TABLE 3

PROPYLENE CONVERSION AND PRODUCT SELECTIVITY VALUES AT VARIOUS TIMES IN THE REACTION CYCLE USING SUPPORTED Bi_2O_3 AT 560°C AND GHSV OF 190

Time (min)	Conversion (mole %)	Selectivity (Mole %)								
		CO_2	Acrolein	2,4-Hexadiene	1,5-Hexadiene	1,3-Hexadiene	1,4-Hexadiene	Benzene	1,3-Cyclohexadiene	1,4-Cyclohexadiene
1	22.55	19.0	5.4	4.1	41.0	2.5	0.8	21.7	3.3	2.2
2	19.70	20.1	3.6	3.9	47.0	3.1	0.3	19.4	2.1	0.5
4	19.07	18.4	4.6	3.3	46.9	3.0	0.6	18.3	3.4	1.5
8	14.78	18.3	4.3	2.8	50.8	3.8	0.5	14.7	3.7	1.2
20	7.18	18.0	3.2	1.7	61.4	5.8	0.4	7.8	1.3	0.4

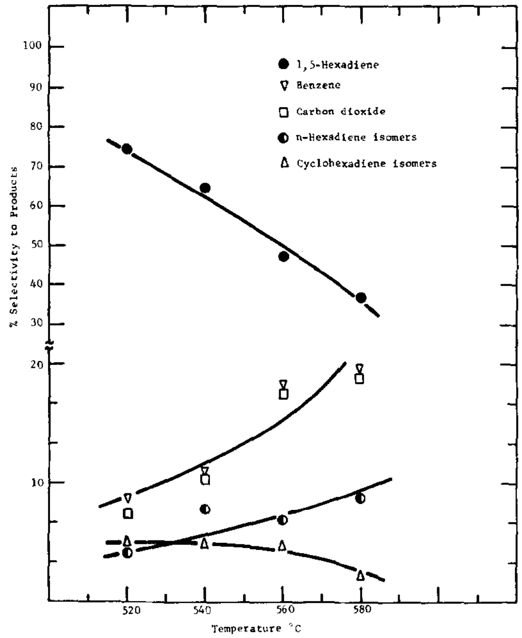


FIG. 6. Variation of product selectivity with temperature using supported Bi_2O_3 at a propylene GHSV of 190.

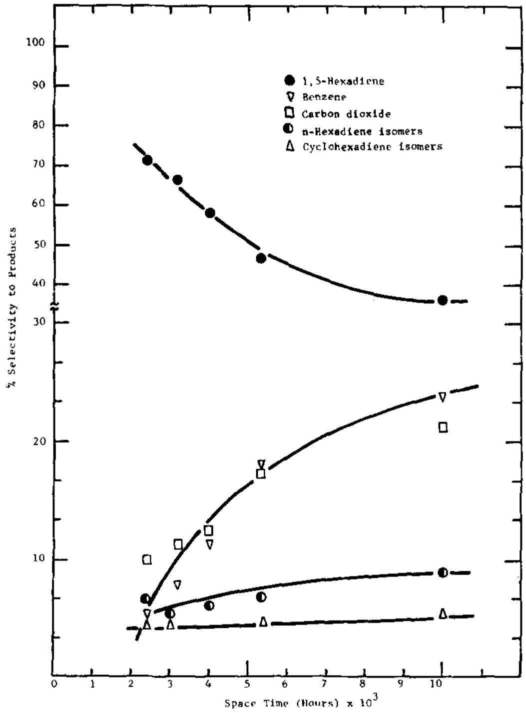


FIG. 7. Variation of product selectivity with space time using supported Bi_2O_3 at 560°C.

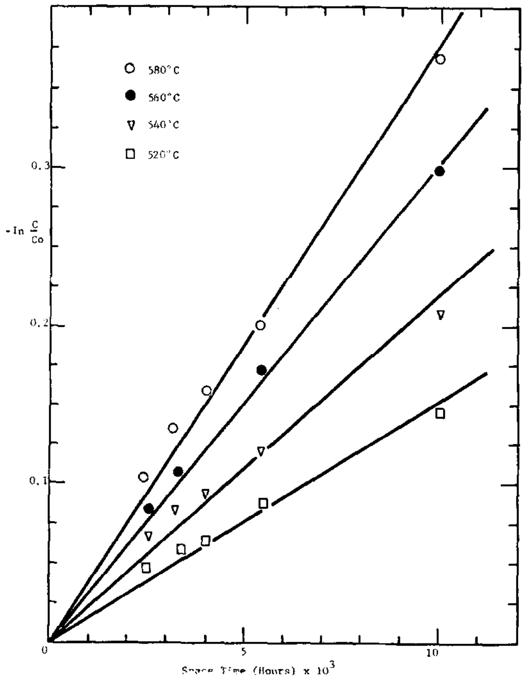


FIG. 8. First order plots using supported Bi_2O_3.

Bismuth Oxide as a Catalyst

Bi_2O_3 can also function as a catalyst for the continuous production of 1,5-hexadiene from a propylene-air mixture. However, under the best conditions required to have Bi_2O_3 truly function as a catalyst, the selectivity was much lower compared to the use of Bi_2O_3 as an oxidant. The best conversion-selectivity values obtained using Bi_2O_3 as the catalyst were 20 and 60%, respectively. Selectivity refers to all the C_6 products, which means that 40% of the propylene converted went to carbon dioxide. The C_6 products consisted of 70% 1,5-hexadiene, 25% benzene, and the remainder a mixture of normal and cyclohexadiene isomers. The conditions used to obtain these values were: 538°C, propylene GHSV of 200 and propylene, oxygen and nitrogen partial pressures of 0.118, 0.047, and 0.835 atm, respectively. This reaction was found to be zero order in oxygen and first order in propylene. The lower selectivity found when gas-phase oxygen is added is most likely due to the reaction of the allylic radicals, either on the surface or in the gas phase with oxygen to form the allyl peroxy

$$C_3H_5\cdot + O_2 \rightarrow C_3H_5O_2\cdot \rightarrow CO_2 \text{ etc.} \quad (1)$$

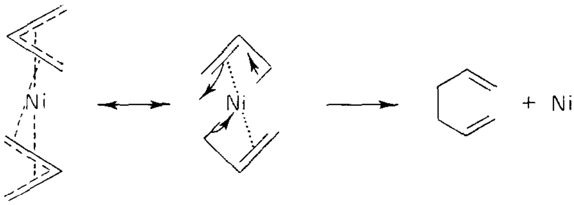
radical which decompose to CO_2 and other undesirable products.

Discussion

The formation of 1,5-hexadiene from propylene using Bi_2O_3 as the oxidant can be considered as a noncatalytic fluid–solid reaction where an unreacted core model applies (*15*). Such a reaction can be visualized as propylene initially reacting with a Bi_2O_3 particle, either on a support or part of a Bi_2O_3 pellet to form gaseous products leaving molten bismuth metal. Additional reaction involves the diffusion of propylene through this molten bismuth to react with more Bi_2O_3. From studies on the reduction of Bi_2O_3 using a microbalance in a flow system (*16*), it has been found that both surface-chemical reaction and diffusion were kinetically important to the overall reaction rate. From these studies, it was determined that the apparent activation energy for the initial surface chemical-controlled reaction was 27 kcal/mole and 20 kcal/mole for the diffusion-limited reaction. The value of 27.5 kcal/mole found in this paper for the unsupported Bi_2O_3 is in excellent agreement with the value found for the surface-chemical reaction from the microbalance measurements, and would be expected since only about 3% of the Bi_2O_3 oxygen has been consumed after 4 min of reaction. For the supported Bi_2O_3, the degree of oxygen consumption is much higher (~18% after 4 min), and because of this, diffusion should start to become important. The lower activation, 21.5 kcal/mole, obtained using supported Bi_2O_3 and compared to a value of 20 kcal/mole obtained from the microbalance studies, indicates that diffusion is important.

The formation of 1,5-hexadiene upon passing propylene over bismuth oxide was an unexpected result, since recently the direct reaction of propylene (*17*) and butenes (*18*, *19*) with Bi_2O_3 has been reported without detection of dimerized products or no activity at all. Many other metal oxides were tested for this reaction, and only five others were found to catalyze the dehydrodimerization to some extent. These oxides are: PbO_2, CdO, TlO, AgO, and ZnO. All were found to be much less reactive and selective than Bi_2O_3. The two most active metal oxides besides Bi_2O_3 were PbO_2, and CdO, and both were easily reduced irreversibly to the metallic state. The use of PbO_2, CdO, TlO and AgO for this reaction was recently disclosed in the patent literature (*5–7*).

It is tempting to postulate that the above metal oxides form organo-metallic type complexes with propylene on the surface which undergoes decomposition to 1,5-hexadiene leaving the metal in a reduced valence state. Such surface complexation and decomposition steps could be visualized to be analogous to the bis-(π-allyl) systems which can give rise to 1,5-hexadiene (*20*, *21*).



(1)

However, in a recent paper on this subject it was reported that a high concentration of allylic radicals exist in the gas phase, and it is the radical termination reaction in the gas phase which is the principal path for dehydrodimer formation (*8*).

The direct dimerization of propylene to 1,5-hexadiene with the formation of hydrogen is not thermodynamically feasible over a wide temperature range. From group contribution calculations (*22*), the free energy values for (2) at 400 and 700°K were determined to be +13.20 and +14.49

kcal/mole, respectively. However, if the reaction,

is carried out oxidatively, it is then very favorable. Calculated free energy values for (3) were determined

to be —40.26 and —35.51 kcal/mole at 400 and 700°K, respectively.

The formation of 1,5-hexadiene by the direct reaction of propylene with Bi_2O_3 as the oxidant is feasible only because the lattice oxygen is reacted with the hydrogen abstracted from the propylene to form water. This abstraction of the allylic hydrogen to give an adsorbed allyl radical is the rate-determining step. The free energy of formation of 1,5-hexadiene according to the following reaction:

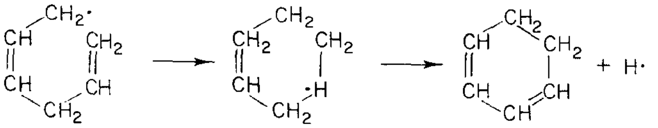
was calculated to be —13.3 kcal/mole at 773°K, showing that it is not as favorable an oxidative process as utilizing gaseous oxygen. Further abstraction of hydrogen from 1,5-hexadiene results in the formation of the 1,5-hexadiene radical which exists in the canonical forms I and II.

$$2\,CH_2{=}CH{-}CH_3 \dashrightarrow CH_2{=}CH{-}CH_2{-}CH_2{-}CH{=}CH_2 + H_2 \tag{2}$$

$$2\,CH_2{=}CH{-}CH_3 + 1/2O_2 \dashrightarrow CH_2{=}CH{-}CH_2{-}CH_2{-}CH{=}CH_2 + H_2O \tag{3}$$

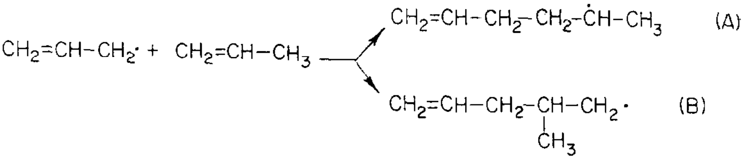
$$6C_3H_6(g) + Bi_2O_3(s) \dashrightarrow 3C_6H_{10}(g) + 2Bi(l) + 3H_2O(g) \tag{4}$$

$$\underset{\text{I}}{CH_2{=}CH{-}\dot{C}H{-}CH_2{-}CH{=}CH_2} \longleftrightarrow \underset{\text{II}}{\cdot CH_2{-}CH{=}CH{-}CH_2{-}CH{=}CH_2} \tag{5}$$

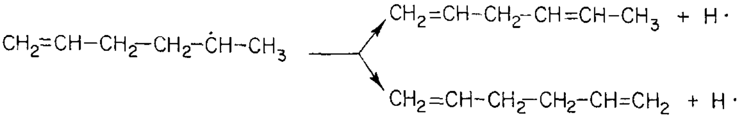


(6)

$$2CH_2{=}CH{-}CH_3\cdot \dashrightarrow CH_2{=}CH{-}CH_2{-}CH_2{-}CH{=}CH_2 \tag{7}$$



$$CH_2{=}CH{-}CH_2\cdot + CH_2{=}CH{-}CH_3 \longrightarrow \begin{cases} CH_2{=}CH{-}CH_2{-}CH_2{-}\dot{C}H{-}CH_3 & (A) \\ CH_2{=}CH{-}CH_2{-}\underset{\underset{\displaystyle CH_3}{|}}{C}H{-}CH_2\cdot & (B) \end{cases} \tag{8}$$



$$CH_2{=}CH{-}CH_2{-}CH_2{-}\dot{C}H{-}CH_3 \longrightarrow \begin{cases} CH_2{=}CH{-}CH_2{-}CH{=}CH{-}CH_3 + H\cdot \\ CH_2{=}CH{-}CH_2{-}CH_2{-}CH{=}CH_2 + H\cdot \end{cases} \tag{9}$$

The formation of the intermediate cyclohexadienes most likely results from the dehydrogenation of the cyclohexenyl radical formed by the intramolecular addition of the II radical.

Benzene is then formed by the highly favorable dehydrogenation of the cyclohexadienes.

Propylene pyrolysis can be ruled out as the source of allyl ($C_3H_5\cdot$) when propylene is passed over Bi_2O_3, because (1) the reaction can take place at 450°C, and allyl is produced via propylene pyrolysis at higher temperatures (*23*), and (2) there is no reaction with many other metal oxides at temperatures up to 600°C.

There are two main possibilities that have to be considered for the formation of 1,5-hexadiene from propylene. The first is a termination reaction of two allyl radicals on the surface and in the gas phase (7) with a net gain of energy of about 42 kcal (*24*).

The other involves the addition of allyl to propylene with a loss of a hydrogen atom as shown in reactions (8) and (9) (*22*). Both 1,5- and 1,4-hexadiene would be formed according to reaction (9). Cyclization of either (A) or (B) leads to the 3-methylcyclopentyl radical which ends up as methyl cyclopentene (*25*). With Bi_2O_3 and propylene no methyl cyclopentene was observed, and only a very small amount of 1,4-hexadiene was formed. The formation of 1,4-hexadiene with Bi_2O_3 is most likely thermally, since its formation slightly increased with increasing temperature. These results indicate that a mechanism where allyl combines with propylene can be ruled out as the source of 1,5-hexadiene.

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