

# Catalytic Oxidations with Sulfur Dioxide

## I. Exploratory Studies

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The catalytic oxidation of a range of compounds, using sulfur dioxide as the oxidant, over a variety of catalysts has been examined. Metal sulfides and metal phosphates were the best of the catalysts examined. The oxidative dehydrogenation of olefins to diolefins proceeds very well, giving much higher yields from the higher olefins than for the corresponding oxidation with oxygen. Interesting reactions of paraffins are isobutane to isobutylene, butane and isopentane to the corresponding thiophenes, hexane to benzene, and 3-methylpentane to vinylthiophene. When cyclization to thiophenes or aromatics is possible, large yields of olefins or dienes cannot be obtained from paraffins. Mesityl oxide is cyclized to 2,4-dimethylfuran quite well but no furan is made from crotonaldehyde.

### INTRODUCTION

The catalytic oxidation of hydrocarbons is quite successful with a number of materials, such as ethylene, propylene, butylene, benzene, and alkyl aromatics, but there are a number of systems, which include desired products as well as desired feeds, where the selectivity of the reaction is either low or practically nonexistent (1). As an example, consider the oxidation over bismuth molybdate of 2-butene and 2-methyl-2-butene (2). Production of butadiene from butylene is a very clean reaction, while the selectivity of oxidation of isoamylene to isoprene is low, especially at high conversion levels.

Olefin conversion (%)	20	40	80
Butadiene selectivity (%)	90	90	85
Isoprene selectivity (%)	73	62	36

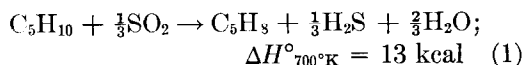
The reduced selectivity for this second reaction is chiefly due to the rapid complete oxidation of the isoprene formed. We have screened 60 catalysts for the oxygen oxidation of isoamylene. A large number of these were quite similar in their performance, among which bismuth molybdate was typical. This is just another example indicating

that catalyst variation, at least for some selected reactions, has been moderately well explored.

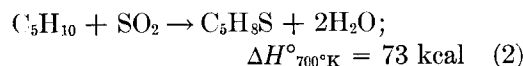
However, of the three components of catalytic oxidation (reductant, catalyst, and oxidant), variations of the oxidant have been examined but little, mainly because air or oxygen is cheap and readily available and other oxidants often lead to undesirable by-products or handling difficulties. Nevertheless, substantial gains in process efficiency may easily warrant consideration of more unconventional oxidants. Of these oxidants, sulfur dioxide is perhaps the most common and easiest handled. The patent literature discloses a number of cases where it is used for oxidative dehydrogenation. Rosen (3) used chromia-alumina catalyst and SO<sub>2</sub> to make isobutylene from isobutane while Stone and Korpi (4) used a supported copper catalyst and SO<sub>2</sub> to form butadiene from butene. Danforth (5) dehydrogenated naphthenes with activated carbon and SO<sub>2</sub>. Murray (6) claims a dehydrogenation process in which feed and SO<sub>2</sub> are passed over an oxide of molybdenum, cobalt, or tungsten until the catalyst is sulfided, then the catalyst is reoxidized back to the oxide. Stringer *et al.* (7) have

claimed high yields of benzene from hexane using SO<sub>2</sub> and a calcium-nickel phosphate catalyst.

Another advantage of using SO<sub>2</sub> for oxidative dehydrogenation is that the reaction is actually endothermic. The following thermodynamic data have been calculated (8) for 2-methyl-2-butene:



As will be seen later, the only major by-product is 3-methylthiophene, formation of which is highly endothermic



The slightly endothermic nature of the oxidative dehydrogenation of isoamylenes with SO<sub>2</sub> allows considerable freedom in reactor design. Large adiabatic reactors would be feasible. No explosive hazards are involved so that no restrictions are imposed on feed composition.

The thermodynamics of reaction (1) are favorable at about 300°C and higher.

Normally liquid feeds were fed by bubbling helium through the liquid thermostated for the desired vapor pressure. The vapor effluent from the reactor, at 200°C, was monitored with a mass spectrometer. Identification of compounds and analyses were done mainly by mass spectrometry and sometimes by gas liquid chromatography (GLC). Confirmation of identification was most often done by comparison with authentic samples. When these were not available, the compounds were isolated by GLC, mass spectra were obtained and any other measurements (NMR, IR, etc.) necessary for identification were made.

In the tables of data, GHSV refers to the total feed gas hourly space velocity (volumes of feed per volume of catalyst per hour), including oxidant and diluents; it is calculated at 0°C and 760 mm Hg. Conversion is percentage of a feed species converted to other materials. Selectivity is the percentage of carbon atoms in a given product relative to carbon atoms in all products. In some of the tables of this paper, not all of the minor products are listed. This accounts

Temp. (°C)	27°	227°	427°	627°
K° <sub>equil</sub> (atm <sup>2/3</sup> )	7.4 × 10 <sup>-5</sup>	4.0 × 10 <sup>-1</sup>	1.3 × 10 <sup>1</sup>	1.4 × 10 <sup>2</sup>

We have found that reaction (1) proceeds with good selectivity at high conversion, in marked contrast to the oxidation with oxygen. We have investigated a number of catalytic reaction systems using sulfur dioxide as oxidizing agent. This report summarizes the work on olefins and paraffins, together with some oxygen-containing compounds. Most of the systems studied have involved individual reactions but a sufficient number have been investigated to give a fairly general treatment. Individual reactions will be treated separately in detail and general statements will be left for the discussion at the end.

#### EXPERIMENTAL

Apparatus and techniques were similar to those used earlier (9). The glass reactor in the continuous flow system contained a small amount of catalyst (usually 2–10 cc, 10–20 mesh) and operated at atmospheric

pressure. Normally liquid feeds were fed by bubbling helium through the liquid thermostated for the desired vapor pressure. The vapor effluent from the reactor, at 200°C, was monitored with a mass spectrometer.

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Catalyst activity was usually not constant, decreasing substantially in a period of hours, due to coke formation. Complete regeneration occurred easily with oxygen but not with sulfur dioxide.

Sulfur balance errors in these runs were erratic and both positive and negative. Large errors appeared after changes of conditions, apparently due to dynamic exchanges of oxygen and sulfur with the solid. These errors usually decreased with time, indicating approach to a steady state condition. That the overall reactions occur according to Eqs. (1) and (2) are shown by the following data obtained on a sulfided bismuth molybdate, after running for some period of time. Under conditions in which 84% of the isoamylenes and 54% of the SO<sub>2</sub> were converted, for every 100 moles of hydrocarbon reacted 66 moles of isoprene

were produced along with 28 moles of methylthiophene, while 24 moles of H<sub>2</sub>S and 128 moles of H<sub>2</sub>O were made. Equations (1) and (2) indicate 22 moles of H<sub>2</sub>S and 100 moles of H<sub>2</sub>O would be formed from the production of the isoprene and methylthiophene. The 6 moles of isoamylene converted to minor by-products would account for some of the additional H<sub>2</sub>S and H<sub>2</sub>O observed.

## RESULTS

### *Isoamylene*

Since bismuth molybdate has been most extensively explored for oxidative dehydrogenation with oxygen, this catalyst was examined in some detail for oxidation with SO<sub>2</sub>. When bismuth molybdate is used in the oxide form with SO<sub>2</sub>, its initial behavior is very similar to that with oxygen. The selectivity is low (essentially identical to that obtained with oxygen), other oxygenated products (C<sub>5</sub>H<sub>8</sub>O and C<sub>5</sub>H<sub>6</sub>O) are formed, and large amounts of CO<sub>2</sub> are formed. In experiments with 2-methyl-2-butene and SO<sub>2</sub> (C<sub>5</sub>/SO<sub>2</sub> = 0.8, GHSV = 600, 550°C), the activity of the catalyst went down markedly with time (hydrocarbon conversion dropped from 86% to 27%, in the first hour). This was probably due to sulfiding of the catalyst, since practically no H<sub>2</sub>S came off the catalyst at first. A rough calculation based on retained sulfur indicated that about 5% of the oxygen in the catalyst had been replaced by sulfur after 1 hr under the above conditions. Since these data indicated that the steady state condition of the catalyst is the sulfide form, a portion was pretreated with H<sub>2</sub>S for 2 hr at 500°C. Gain in weight indicated that about one-half of the bulk oxygen had been replaced with sulfur. Retreating of this catalyst with 2-methyl-2-butene showed that selectivity is markedly improved over that of the oxide form; isoprene plus methylthiophene are about 90%. Practically no oxygenated compounds were formed, not even CO<sub>2</sub>. The activity, although low, was fairly steady, compared to the rapid decline for the oxide form (conversion dropped from 26% to 23% in 45 min).

More extensive data for another sulfided

bismuth molybdate are shown in Fig. 1. These data were obtained under a variety of conditions but they form a consistent pattern. This catalyst contained more molybdenum (Bi, 2Mo) than the one above (Bi, Mo). The line without points represents oxidation with oxygen over bismuth molybdate at 460°C. Use of sulfur dioxide instead of oxygen results in much better selectivity to isoprene. Selectivity is better than 80% at 40% conversion and is 65% at 85% conversion. Methylthiophene is the only major by-product. It is undoubtedly produced as a subsequent reaction of the isoprene formed since methylthiophene selectivity increases markedly with increasing conversion. The selectivity of a given conversion did not appear to vary in the temperature range 500–600°C. A small amount of oxygen was added to the feed in the hope of increasing the activity or reducing the methylthiophene selectivity with the results in the following table.

EFFECT OF ADDED O <sub>2</sub>					
C <sub>5</sub> H <sub>10</sub> /O <sub>2</sub> = 4, SO <sub>2</sub> /O <sub>2</sub> = 4, 600°C					
O <sub>2</sub> added	C <sub>5</sub> H <sub>10</sub> conv. (%)	Selectivity (%)			
		Isoprene	Methylthiophene	CO <sub>2</sub>	CO
Yes	38	70	3	5	3
No	37	74	5	1	1

Methylthiophene was reduced somewhat, but isoprene selectivity was also reduced due to increase in CO<sub>2</sub> and CO. There was no increase in activity even after 5 hr operation. In other tests with other catalysts, large amounts of oxygen only produced larger amounts of CO<sub>2</sub>, with no beneficial effects.

The bismuth molybdate catalysts discussed above have low surface areas, a few square meters per gram, and their activity in the sulfided form is low. A catalyst which should have had a larger active surface was examined in an attempt to obtain increased activity. This catalyst was made by pretreating with hydrogen sulfide a bismuth phosphomolybdate (12Bi, P, 12Mo) on silica catalyst which had a surface area, before sulfiding, of 99 m<sup>2</sup>/g. However, this

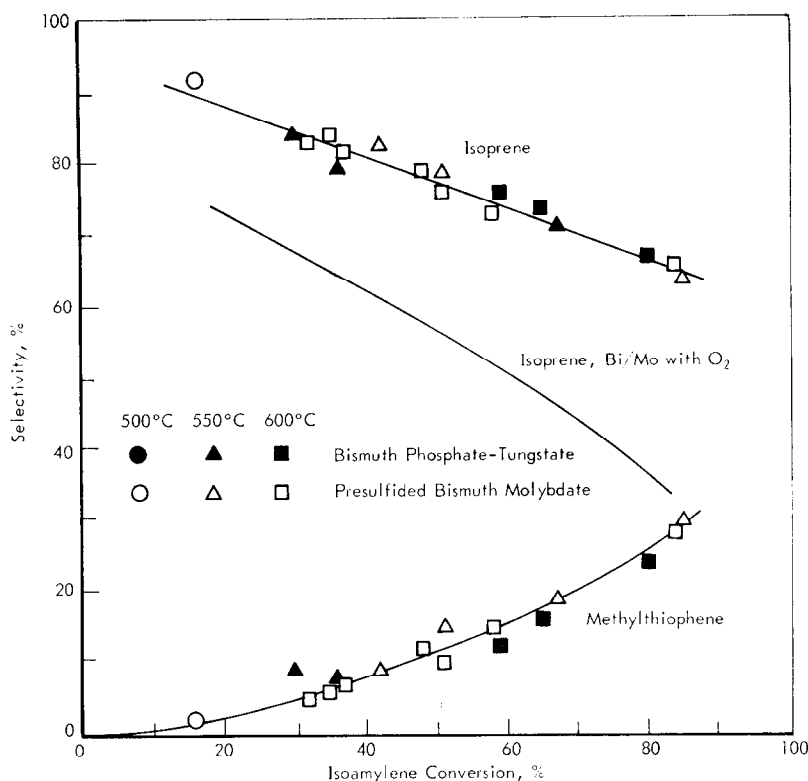


FIG. 1. Oxidation of 2-methyl-2-butene with  $\text{SO}_2$  over bismuth phosphate-tungstate and presulfided bismuth molybdate.

catalyst was no more active than the unsupported catalysts. Figure 2 shows how the activity of this catalyst changes with time. There is a slow steady decline in activity, due to coke buildup on the catalyst. Attempts to regenerate the catalyst with  $\text{SO}_2$  were unsuccessful. The coke can be burned off with oxygen, care being taken to prevent overoxidation of the sulfide to the oxide, and the activity restored to normal, as shown in Fig. 2. (The lower conversion for the regenerated catalyst in Fig. 2 is due to the increased space velocity.) Attempts at reducing the coke buildup by adding oxygen to the feed have not been successful, as shown in Fig. 2. The amount of oxygen added in Fig. 2 was sufficient to lower the isoprene selectivity by about 2% without affecting the decline in activity. Increased amounts of oxygen merely resulted in further burnup. These results are typical of the various catalysts examined in this work. Although not all of the catalysts have

shown the simple decline curves of Fig. 2, activities have sometimes been erratic and hard to reproduce. In our screening work here we have been more concerned with selectivity at a given conversion and have not investigated activity stability for all the catalysts examined.

Bismuth phosphotungstate differs from bismuth molybdate in one respect: its selectivity behavior in the oxide form. Figure 1 shows a conversion selectivity plot for a high phosphorus bismuth phosphotungstate (30Bi, 13P, 12W) used in the oxide form with  $\text{SO}_2$ . Selectivity is the same as for presulfided bismuth molybdate. The phosphotungstate makes only a small amount (1–8%) of  $\text{CO}_2$  compared to the molybdate. This would indicate low bulk oxygen mobility for the phosphotungstate. When large amounts of oxygen are added to the feed for the phosphotungstate,  $\text{CO}_2$  increases markedly (17% selectivity to  $\text{CO}_2$  when  $\text{O}_2/\text{SO}_2 = 0.3$ ).

The initial activity behavior for the phos-

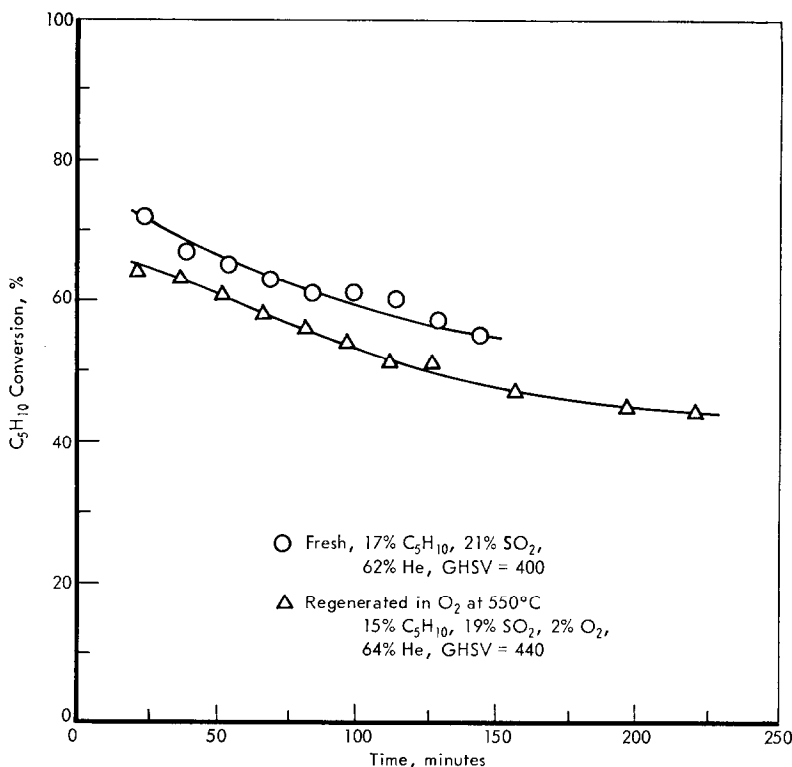


Fig. 2. Oxidation of 2-methyl-2-butene with SO<sub>2</sub> over sulfided bismuth phosphomolybdate on silica at 550°C.

photungstate was somewhat erratic, followed by a steady decline. To separate the effects of sulfiding and coking, a bismuth tungstate was presulfided by calcining in H<sub>2</sub>S and examined for oxidation with SO<sub>2</sub>. Activity declined steadily with the catalyst, somewhat faster than that for sulfided bismuth molybdate in Fig. 2. The behavior of bismuth tungstate is very similar to bismuth molybdate in selectivity when both are sulfided. The tungstate is more selective in the oxide form and declines faster in activity when in the sulfide form.

When bismuth molybdate or tungstate is sulfided there is no assurance that the resulting solid is not a mixture of single metal sulfides. We, therefore, examined bismuth sulfide, molybdenum sulfide, tungsten sulfide, and nickel sulfide as oxidation catalysts. Bismuth sulfide was quite active and selective except that methylthiophene selectivity was high at 500° and 550°C. However, at 600°C selectivity to isoprene

was 76% at 75% conversion. With the molybdenum sulfide extensive amounts of methylthiophene were also produced at 500°C, but at 600°C isoprene was made with selectivity equal to that obtained with the sulfided bismuth molybdenum or tungsten catalysts (75% selectivity at 69% conversion). Furthermore, the activity was quite high, due either to a higher surface area or to a higher intrinsic activity. Tungsten sulfide and nickel sulfide are slightly less selective but quite active.

A number of other catalysts were examined, and examples of the results obtained are listed in Table 1. Quite a few of these were only slightly less selective than those discussed above. Calcium nickel phosphate was quite good, especially at 600°C. Metal phosphates in general were good and required no presulfiding. A bismuth-tin-iron-tungstate-molybdate and a bismuth phosphate gave selectivities to isoprene of about 80% at 30-40% conver-

TABLE 1  
 OXIDATION OF 2-METHYL-2-BUTENE WITH SO<sub>2</sub>

Catalyst	Total GHSV (STP)	C <sub>4</sub> /SO <sub>2</sub>	Temp. (°C)	Conversion (%)		Selectivity (%)	
				SO <sub>2</sub>	C <sub>4</sub> H <sub>10</sub>	C <sub>4</sub> H <sub>8</sub>	C <sub>4</sub> H <sub>6</sub> S
				Atmospheric pressure, C <sub>4</sub> /He = 0.28; rest of feed is SO <sub>2</sub> ; rest of by-products are mainly CS <sub>2</sub> , COS, CO <sub>2</sub> , CO			
Bi, Mo oxide	600	0.8	550°	28	27	65	13
Bi, Mo sulfide	900	1.8	550°	23	24	83	7
Bi, 2Mo sulfide	400	0.2	550°	14	85	64	30
Bi, 2Mo sulfide	1100	0.8	600°	14	35	84	6
12Bi, P, 12Mo/50% SiO <sub>2</sub> S <sub>s</sub> = 99 m <sup>2</sup> /g, calc in H <sub>2</sub> S	400	1.0	550°	31	61	70	17
30Bi, 13P, 12W oxide	600	0.9	540°	14	30	84	10
	600	0.9	600°	45	80	67	24
Bi, W sulfide	230	1.4	550°	28	47	81	10
	230	1.4	600°	27	50	76	9
Bi sulfide/35% SiO <sub>2</sub>	1000	0.9	500°	39	53	53	42
	1000	0.9	550°	47	70	66	29
	1000	0.9	600°	46	75	76	17
Mo sulfide/75% SiO <sub>2</sub>	240	2.5	500°	100	47	28	61
	1700	2.4	550°	82	62	72	22
	1700	2.5	600°	94	69	75	17
W sulfide/30% SiO <sub>2</sub>	2800	0.9	550°	24	42	70	19
Ni sulfide/81% SiO <sub>2</sub>	360	2.0	550°	99	70	57	33
4 Bi, 4Sn, 4Fe, 4W, 6Mo oxide	1100	1.2	550°	72	76	61	27
	1100	1.5	600°	28	26	83	5
19% Cr <sub>2</sub> O <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub>	600	0.5	325°	43	81	4	86
	1100	1.0	320°	32	31	22	65
	1100	1.0	495°	89	63	29	41
2Cr, Cu, Zn oxide	450	1.0	550°	38	37	73	7
BiPO <sub>4</sub>	230	1.3	550°	22	43	79	8
	230	1.3	600°	14	39	76	2
Ni <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> ·7.1Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	490	1.5	500°	38	45	70	23
	490	1.6	550°	61	67	71	20
	550	1.5	600°	79	85	67	22
	1100	0.7	600°	25	64	76	13
In PO <sub>4</sub>	1600	1.5	550°	12	22	92	0.3
	200	1.6	600°	11	61	58	2
Ag <sub>3</sub> PO <sub>4</sub>	1200	1.1	460°	2	17	61	0
Quartz chips	600	1.1	545°	6	6	62	14
	600	1.5	600°	8	8	80	5
	600	1.5	650°	14	31	69	6

sion. A chromia-copper-zinc oxide catalyst gave fairly good selectivity to isoprene but its activity was low and decreased rapidly. Silver phosphate was relatively inactive and unselective. Indium phosphate was unusual in that very little methylthiophene was produced. However, 4-8% selectivity to isopentane was found, along with substantial amounts of butylene and methane.

Activity, although low, was substantially above "thermal" (quartz chips, Table 1). Furthermore, quartz chips did not produce the isopentane found with the indium phosphate. Chromia on alumina produced large amounts of methylthiophene, especially at lower temperatures. At 325°C, selectivity to methylthiophene was 86% at isoamylene conversion of 81%.

All of the preceding experiments were made using 2-methyl-2-butene. Some runs were also made with 2-methyl-1-butene, using a molybdenum sulfide catalyst. A comparison of these data with those for 2-methyl-2-butene with the same catalyst showed no difference in the behavior of the two isomers. The likely possibility of double bond isomerization was not checked.

### Butylene

1-Butene was oxidized with  $\text{SO}_2$  over a bismuth phosphate-tungstate catalyst (30Bi, 13P, 12W). The results are shown in Fig. 3. In general, the results are quite analogous to those obtained with isoamylene. Butadiene is made in quite high selectivity, thiophene is the only major by-product and its selectivity increases markedly with olefin conversion. Activity again declines with time, due to coking. Butadiene selectivity is a few percentage points below that ob-

tained with bismuth molybdate and oxygen, the difference being about equivalent to the amount of butadiene converted to thiophene with  $\text{SO}_2$  oxidant.

### Propylene

Propylene was oxidized with sulfur dioxide with two catalysts. The bismuth phosphate-tungstate catalyst (30Bi, 13P, 12W) which was quite active and selective with isoamylene and butylene had very little activity for the oxidation of propylene and produced primarily carbon oxides. A bismuth molybdate catalyst was then tested and the results are shown in Table 2. The catalyst was quite active initially, but declined rapidly with time. No sulfur-containing organic compounds were detected. Selectivity to acrolein improved with time. The amount of acrolein produced remains constant with time, indicating the possibility of two parallel reactions, one of which produces acrolein steadily, while the

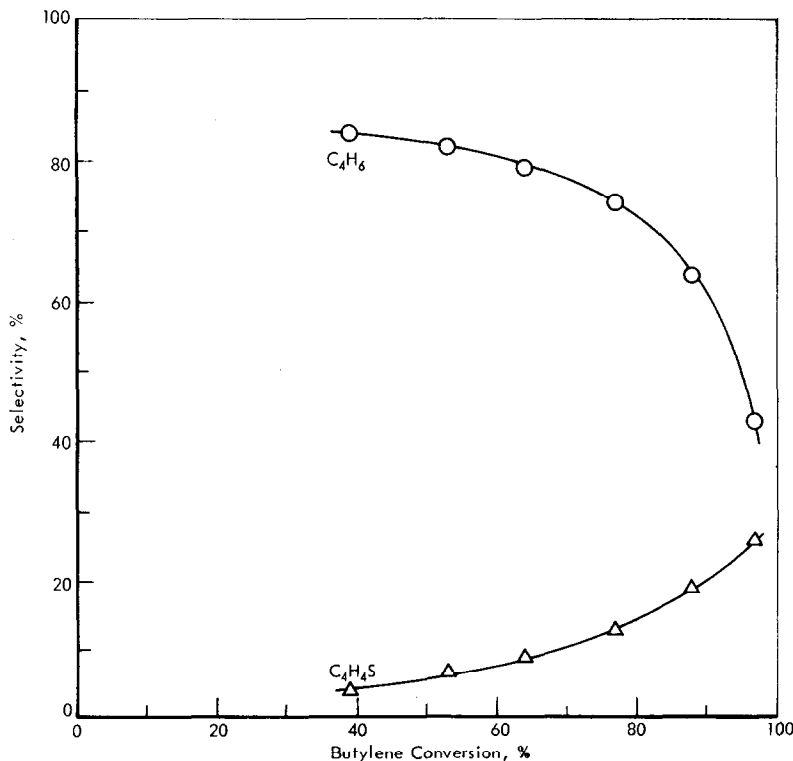


FIG. 3. Oxidation of 1-butene over bismuth phosphate-tungstate with  $\text{SO}_2$ ;  $550^\circ\text{C}$ , GHSV = 600, catalyst age 50-240 min.

TABLE 2  
OXIDATION OF PROPYLENE WITH SULFUR DIOXIDE

Time (min)	C <sub>3</sub> H <sub>6</sub> conversion (%)	C <sub>3</sub> H <sub>4</sub> O selectivity (%)	Yield per pass (%)
5	99.7	10	10
20	82	18	15
35	39	34	13
55	30	44	13
75	26	52	13
105	22	57	13

other produces carbon oxides but declines with time.

#### *Isobutylene*

Fresh iron-calcium phosphate gave complete combustion of this olefin. After the catalyst became sulfided, reaction ceased. Practically no reaction was obtained with molybdenum sulfide at 450-550°; the small amount of products formed consisted of oxides and sulfides of carbon.

#### *Propane*

Reaction of this compound is very slow and not selective; the main products are those of complete combustion. Propylene was the only noncombustion product found. With calcium-nickel phosphate (GHSV = 90) at 550°C, selectivity to propylene was only 14% at 31% propane conversion. With molybdenum sulfide (GHSV = 370 after 100 min and 60 min, respectively) at 500°C, selectivity to propylene was 54% at 11% conversion and 30% at 16% conversion. These results may occur in two ways: the initial propane reaction may be unselective or the propylene product may be very susceptible to combustion. The following results tend to eliminate the latter. Calcium-nickel phosphate is a good and active catalyst for forming isothiazole from propylene, ammonia, and sulfur dioxide. Ammonia added to propane-SO<sub>2</sub> over this phosphate catalyst should scavenge the propylene formed and prevent its combustion. Such a reaction was tried over both calcium-nickel phosphate and molybdenum sulfide and in no case was the combustion

diminished. It thus appears that the initial reaction of the propane itself is not selective.

#### *n-Butane*

Several catalysts were examined for the oxidation of butane with sulfur dioxide. Desired reactions were oxidative dehydrogenation to butylene or butadiene and cyclization to thiophene. Unfortunately, no catalyst tested was highly selective. Highest yield of butylene plus butadiene was obtained with a bismuth-iron phosphate catalyst (38% selectivity to butylene plus butadiene at 86% conversion of butane at 600°C and 240 GHSV, 22% selectivity to thiophene). Highest selectivity to butylene plus butadiene was obtained with nickel molybdate (48% selectivity at 52% conversion at 550°C and 200 GHSV, 22% selectivity to thiophene). The highest yield of thiophene was obtained with molybdenum sulfide (64% selectivity at 71% conversion at 550°C and 90 GHSV, 3% selectivity to butylene plus butadiene). The following catalysts were fairly selective to butylene and butadiene: bismuth-iron phosphate, nickel molybdate, calcium-iron phosphate, calcium-nickel phosphate, calcium-iron-nickel phosphate, indium phosphate, bismuth phosphate, indium molybdate, and molybdenum sulfide. The following catalysts were moderately selective to thiophene: molybdenum sulfide, tungsten sulfide, nickel sulfide, calcium-nickel phosphate, bismuth phosphate, vanadium pentoxide-potassium sulfate, and indium molybdate. Catalysts showing activity but poor selectivity were chromia on alumina, cobalt molybdate, bismuth titanate, and a platinum-palladium alloy on Alundum. Inactive catalysts were silver phosphate, platinum on Alundum, copper oxide (ex mirror) on Alundum, and quartz chips.

The main feature preventing high conversion to olefin is the further reaction to thiophene. Butane was oxidized over several catalysts (bismuth-iron phosphate, bismuth phosphate, nickel molybdate, indium molybdate, phosphomolybdic acid; GHSV = 90-480, 410-640°C) with oxygen instead of sulfur dioxide to prevent this further reaction. A comparison of these results with



those with sulfur dioxide shows that in all cases the selectivity to unsaturated hydrocarbons was less with the oxygen than with the sulfur dioxide.

### *Isobutane*

This paraffin with its tertiary hydrogen should react more easily than propane or butane. Furthermore, thiophene formation cannot occur. Isobutane was oxidized over molybdenum sulfide at 500° and 600°C. No effect of temperature was noted. The results are given in Table 3. Isobutylene was formed

TABLE 3  
ISOBUTANE OXIDATION WITH SULFUR DIOXIDE

Molybdenum sulfide catalyst; $P_{C_4H_{10}} = P_{SO_2} = 0.5$ atm				
Time (min)	GHSV	Temp. (°C)	$C_4H_{10}$ conv. (%)	$C_4H_8$ selectivity (%)
15	740	500°	16	74
30	370	500°	20	72
45	370	600°	50	61
60	740	600°	26	70
75	740	600°	18	74
90	740	600°	14	73

in moderate selectivity (70% at 26% conversion and 61% at 50% conversion). The other carbon-containing products were oxides and sulfides of carbon.

### *Isopentane*

This compound was oxidized with sulfur dioxide over two catalysts at 450–550°C. Iron-calcium phosphate initially gave high conversions to  $CO_2$ , but became substantially more selective upon partial self-

sulfidation. A selectivity to methylthiophene of 55%, with 7% selectivity to isoamylene and isoprene at 28% isopentane conversion was obtained at 500°C. Molybdenum sulfide was more selective: 61% selectivity to methylthiophene and 28% selectivity to isoamylene and isoprene at 48% conversion was obtained at 550°C. Other conditions were examined for increased dehydrogenation without cyclization but methylthiophene was always predominant. This paraffin can be oxidized quite selectively to olefin and diolefin but thiophene formation is so fast that high selectivity to the former cannot be obtained.

### *n-Hexane*

A patent to Stringer, Kimberlin, and McQuaid (?) has claimed high conversions and selectivities of *n*-hexane, cyclohexane, and *n*-heptane to aromatics using sulfur dioxide with a calcium-nickel phosphate catalyst. We have verified these claims and have found other catalysts equally good or better.

A summary of the best results obtained with the various catalysts is given in Table 4. The major product other than benzene is hexene, which could be recycled or converted *in situ* with additional sulfur dioxide and longer residence time. Diolefin and triene occur in only minor amounts, presumably due to their high reactivity for cyclization. Thiophene formation also is usually small as is combustion. Temperature in the range 450–600°C has little effect on selectivity. It is surprising that selectivity

TABLE 4  
OXIDATION OF *n*-HEXANE WITH SULFUR DIOXIDE—SUMMARY OF CATALYSTS

Catalyst	Temp. (°C)	GHSV	$C_6H_{14}$ conv. (%)	Selectivity (%)		
				$C_6H_6$	$C_6H_{12} + C_6H_{10} + C_6H_8$	Other
Calcium-nickel phosphate	550°	150	93	58	28	14
Indium phosphate	500°	240	68	74	14	10
Bismuth-iron phosphate	500°	300	44	67	17	16
Molybdenum sulfide	550°	400	68	58	26	16
Bismuth phosphate	550°	150	63	41	39	19
Bismuth-molybdenum sulfide	550°	160	55	36	42	21
Bismuth-tungsten sulfide	550°	320	62	43	27	31
Bismuth sulfide	550°	380	74	41	28	30
Calcium-iron phosphate	550°	1700	72	46	19	35

TABLE 5  
OXIDATION OF 2-METHYLPENTANE WITH SULFUR DIOXIDE

GHSV	Temp. (°C)	$C_6H_{14}$ conv. (%)	Selectivity (%)			
			$C_6H_8S$	$C_6H_{12} + C_6H_{10}$	$C_6H_6S$	$CS_2 + COS$
$P_{C_6H_{14}} = 0.18, P_{SO_2} = 0.41$						
<i>Molybdenum sulfide</i>						
230	500	19	33	13	6	48
230	550	35	19	8	9	64
<i>Calcium-nickel phosphate</i>						
910	550	34	24	42	15	19
450	550	51	24	27	21	23
230	550	66	15	18	19	49

to olefin was roughly independent of conversion.

The highest selectivity to benzene with calcium-nickel phosphate catalyst was 58%. Indium phosphate gave 74% and bismuth-iron phosphate 67%. Several of the other catalysts are only marginally less selective when hexene is also considered.

#### *Methylcyclopentane*

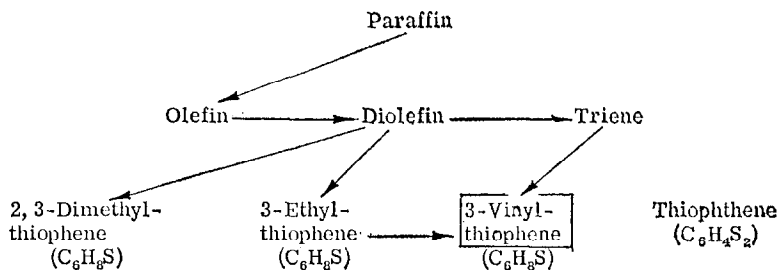
This compound was examined for two purposes: behavior of the  $C_5$  ring in this system and the possibility of ring expansion. Oxidations with sulfur dioxide were carried out over a sulfided bismuth-iron phosphate catalyst at 450°-600°C. No compounds of interest were made to any appreciable extent. At 550°C and GHSV = 400, about 75% of the hydrocarbon was converted; of the amount converted, about 70% did not come out of the reactor and presumably went to coke on the catalyst. Selectivity to  $C_6$  unsaturated compounds was about 4% with the remainder being combustion products. Thus, there was no ring expansion and the  $C_5$  ring system went to coke, a typical behavior for this structure type.

#### *2-Methylpentane*

In analogy with isopentane and 3-methylpentane below, it was anticipated that 2-methylpentane should produce 2,4-dimethylthiophene ( $C_6H_8S$ ) in high yields, since it has the branched structure for reactivity and can cyclize to only one product. Such was not the result. Data are given in Table 5 for two catalysts. With molybdenum sulfide, a surprising amount of combustion occurred, with the best selectivity to dimethylthiophene being 33% at 19% conversion. With calcium-nickel phosphate, combustion was only moderate but dealkylation became important. The best selectivity to dimethylthiophene was 24% at 51% conversion. In comparison with isopentane and 3-methylpentane, 2-methylpentane is less reactive and less selective than expected.

#### *3-Methylpentane*

A substantial effort was spent on the sulfur dioxide oxidation of this compound in attempts to prepare vinylthiophene as an analog of styrene for polymers (10). The relative complexity of such a reaction may be visualized from the following scheme, all steps of which appear to be significant:



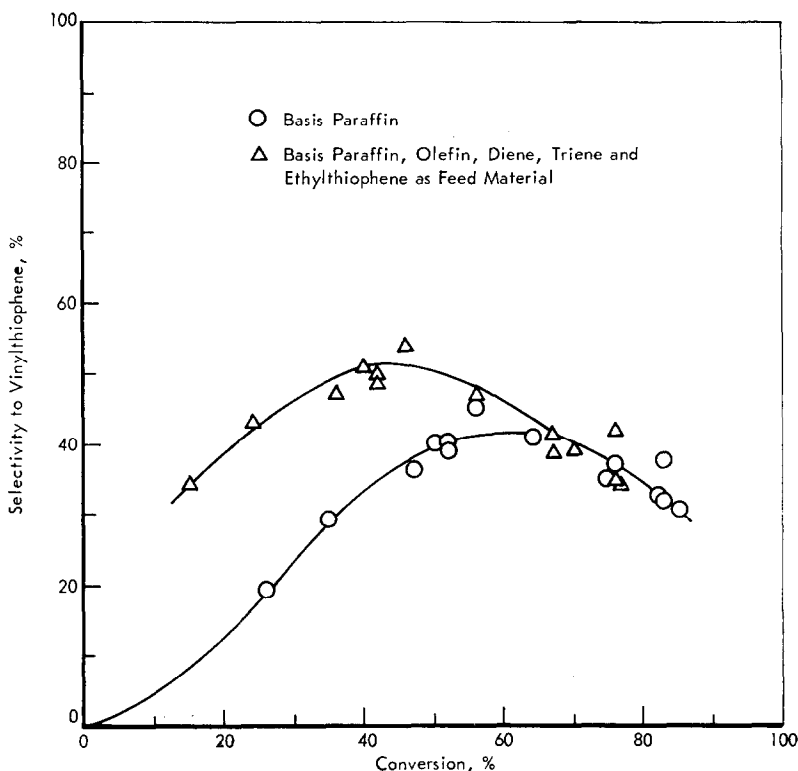


FIG. 4. Formation of vinylthiophene from 3-methylpentane; calcium-nickel phosphate, 550°C.

Further complications are caused by general combustion and dealkylation of the substituted thiophene products. Thiophthene is an analog of naphthalene, consisting of two fused thiophene rings.

Several catalysts were tried for this reaction and the best was calcium-nickel phosphate. Optimum temperature appeared to be about 550°C. Conversion-selectivity data at this temperature are shown in Fig. 4 where the circles give conventional values based on the amount of paraffin converted. These results are typical for a material made from an intermediate product and also susceptible to further reaction. A broad maximum in selectivity (at slightly above 40%) occurs between 50% and 70% paraffin conversion. Some of the products are precursors to vinylthiophene and when these (olefin, diene, triene, and ethylthiophene) are considered to be recycle feed material, the maximum selectivity to vinylthiophene is slightly over 50%, as shown by the triangles of Fig. 4. Figure 5 shows

smoothed curves for conversion-selectivity for the various products formed. Unsaturated hydrocarbons, mostly olefin, are formed at first, followed by vinylthiophene formation. This compound then forms thiophthene. Combustion and dealkylation are moderately constant. For such an assembly of competing and consecutive reactions, selectivity to a particular intermediate is quite sensitive to catalyst and conditions.

Catalyst activity is not constant, as shown in Fig. 6. Activity is moderately constant for an hour or two, followed by a steady decline in activity. Maximum SO<sub>2</sub> conversions in Fig. 6 were 80%, so the initially constant activity is not caused by oxidant depletion. This loss in activity is presumably due to coke formation since regeneration with oxygen, in which carbon dioxide is produced, restores the activity. Attempts at regeneration with sulfur dioxide were not successful.

Several other catalysts were tried for

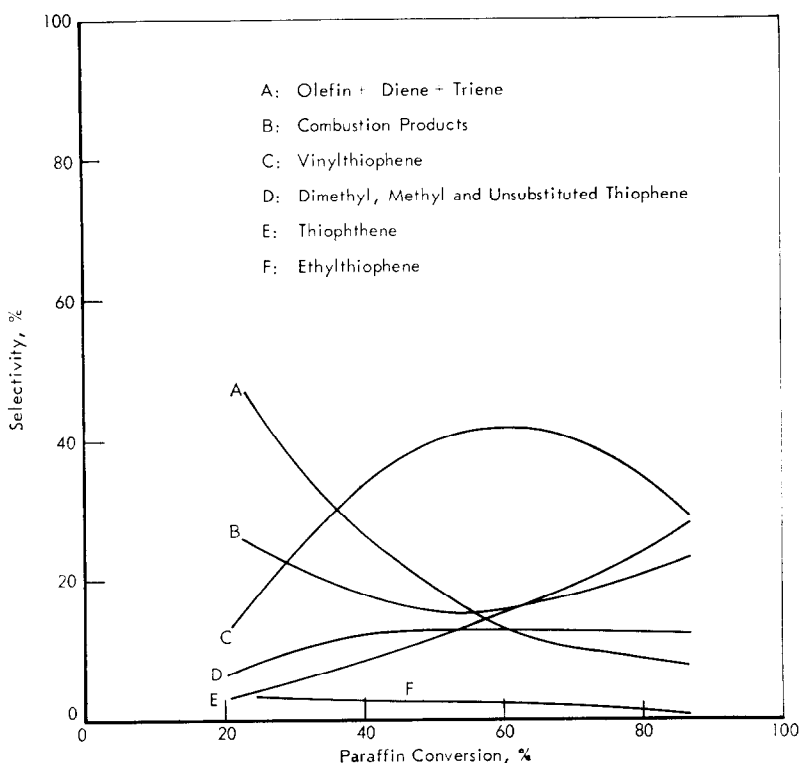


FIG. 5. 3-Methylpentane oxidation over calcium nickel phosphate at 550°C.

this reaction. Table 6 gives a summary of the best results obtained with each catalyst. None was as selective as calcium-nickel phosphate although several

(bismuth-tungsten sulfide, molybdenum sulfide, bismuth-iron phosphate, bismuth phosphate, and cobalt phosphate) gave selectivities to vinylthiophene of over 30%.

TABLE 6  
OXIDATION OF 3-METHYLPENTANE WITH SULFUR DIOXIDE—SUMMARY OF CATALYSTS

Catalyst	Paraffin conv. (%)	Selectivity (%)					
		Vinylthiophene	Ethylthiophene	Olefin + diene + triene	Thiophthene	H, methyl, and dimethylthiophene	CS <sub>2</sub> + COS + CO <sub>2</sub> + CO
Ca, Ni, PO <sub>4</sub>	64	41	2	11	17	13	16
BiWS	74	36	2	10	20	8	24
MoS <sub>2</sub>	21	34	6	19	12	22	7
NiMoS/Al <sub>2</sub> O <sub>3</sub>	30	7	4	9	9	9	62
CoMoS/Al <sub>2</sub> O <sub>3</sub>	20	10	10	15	3	21	40
Bi, Fe, PO <sub>4</sub>	68	33	3	17	18	8	22
Bi PO <sub>4</sub>	33	31	5	11	21	17	15
Co <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	38	30	4	17	14	17	19
InPO <sub>4</sub>	24	22	5	21	5	24	22
Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	37	20	4	14	4	13	46
VPO <sub>4</sub>	51	14	4	14	10	34	25
NdPO <sub>4</sub>	62	14	3	9	21	7	47
CrPO <sub>4</sub>	10	6	11	53	0	6	24
FePO <sub>4</sub>	17	4	1	58	0	12	23
CePO <sub>4</sub>	25	1	2	31	3	9	55

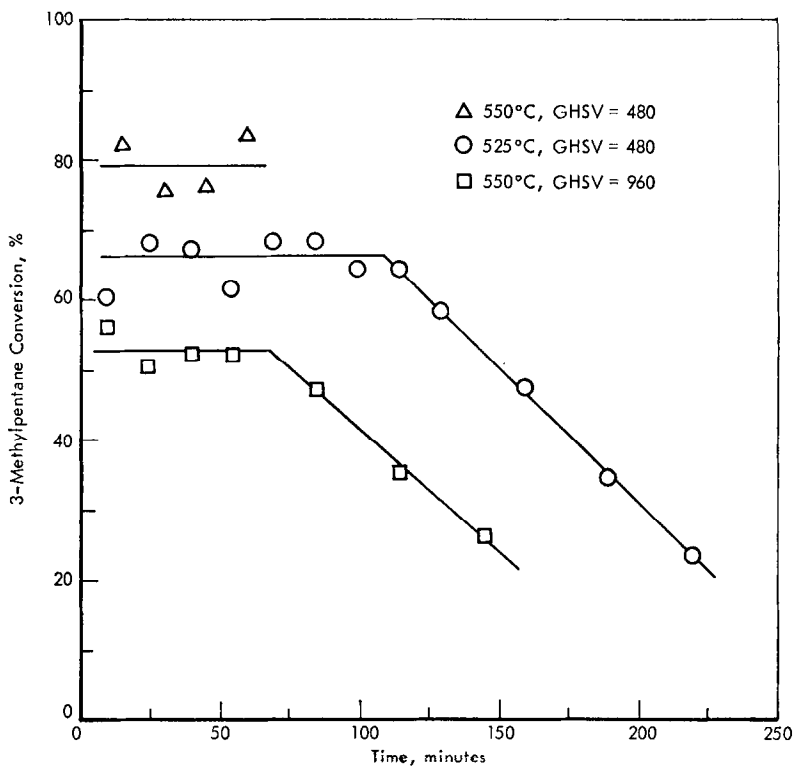


FIG. 6. Calcium-nickel phosphate activity with time.

### *3-Methyl-1-pentene*

The results obtained above indicate that olefin is an intermediate in the formation of vinylthiophene from 3-methylpentane. 3-Methyl-1-pentene was oxidized with sulfur dioxide over several catalysts. As with the paraffin, calcium-nickel phosphate was the best catalyst. At 550°C and 490 GHSV, olefin conversion was 83%.

Although data at low conversions were not obtained, the olefin does not appear to be more reactive than the paraffin. Smoothed conversion-selectivity data for the olefin over calcium-nickel phosphate at 550°C are given in Fig. 7. The major product is diolefin until very high conversion is reached. Highest selectivity to vinylthiophene was 37% at 95% olefin conversion. Figure 7 indicates that this selectivity cannot go too much higher since the amounts of vinylthiophene precursors are becoming quite low. A major source of selectivity loss is the formation of dimethylthiophene, presumably through cyclization of the

diene. Although 3-methyl-1-pentene may not be entirely representative of the olefin intermediates in the oxidation of the paraffin the major selectivity differences (in the olefin vs. paraffin feed) may be due to the much higher concentration of diene intermediate when olefin is fed. If this is true, the kinetics for the various consecutive and parallel reactions must be different. Various amounts of oxygen were added to the feed in some of these experiments, primarily to decrease the rate of catalyst decline due to coking, but this oxygen went quickly to complete combustion and even massive amounts failed to stabilize activity, while increasing selectivity to combustion products substantially.

### *3-Ethyl-1-pentene*

In analogy with other results, this compound should form 2-methyl-3-vinylthiophene in good selectivity. Ring closure can occur in only one way and the formation of the bicyclic dithiophene from the vinyl

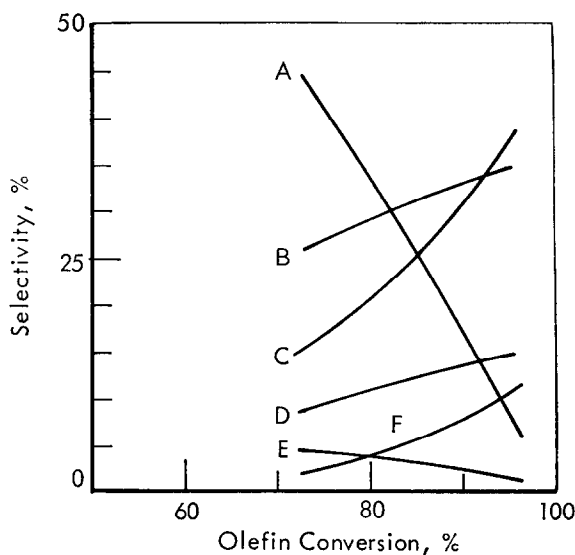


FIG. 7. Oxidation of 3-methyl-1-pentene with sulfur dioxide calcium-nickel phosphate, 550°C. A, olefin + diene + triene; B, combustion products; C, vinylthiophene; D, dimethyl, methyl, unsubstituted thiophene; E, thiophene; F, ethylthiophene.

compound would involve attack at the quite unreactive 4-position. 3-Ethyl-1-pentene was oxidized with  $\text{SO}_2$  over three catalysts in the range 450-550°C. In all cases activity declined very rapidly. Also very large losses, either to coke or polymer, occurred whenever the conversion was high. One of the major products was a surprise: toluene with calcium-nickel phosphate and olefin conversion of 47%, the selectivity to diolefin was 34%, toluene 30%, methylethylthiophene 15%, methylvinylthiophene 18%, and carbon disulfide 3%. No evidence for appreciable amounts of the bicyclic  $\text{C}_7\text{H}_6\text{S}_2$  compound was found in any of these experiments. Bismuth-iron phosphate, at 33% conversion, gave selectivity to diolefin of 55%, toluene 30%, methylethylthiophene 7%, methylvinylthiophene 6%, and carbon disulfide 2%. Molybdenum sulfide gave comparable product distribution but losses were much greater.

The formation of toluene and the large losses may be expected if cyclic  $\text{C}_5$  intermediates are postulated, but this type of reaction has not been evident in other studies in this system. 3-Methyl-1-pentene did not show large losses or formation of

benzene, nor was toluene noted in the oxidation of 3-ethyl-1-pentene over bismuth molybdate with oxygen (2). This is another illustration of the complexity of the catalytic oxidation of hydrocarbons with  $\text{SO}_2$ .

#### *n*-Dodecane

This compound was examined to extend paraffin oxidation into the large molecule range. Homocyclic aromatization and thiophene formation are likely reactions of long-chain molecules. Dodecane was oxidized with sulfur dioxide over two catalysts at 500-600°C. Surprisingly, very little thiophene or combustion occurred. However, olefins were not made in high selectivity. With calcium-nickel phosphate at 550°C, GHSV = 1100 and paraffin conversion of 36%, the selectivity to olefins was 31%, 13% to diolefins, 29% to aromatics, and 28% to cracked products. With molybdenum sulfide at 600°C, GHSV = 1100 and paraffin conversion of 48%, the selectivity to olefins was 24%, 34% to diolefins, 26% to aromatics, and 24% to cracked products. The aromatics are lower with dodecane than with smaller chain length but still quite appreciable. Cracking is also substantial.

*Crotonaldehyde*

The oxidative cyclization of crotonaldehyde to furan with oxygen as oxidant proceeds with fair selectivity (11). This reaction was also examined with sulfur dioxide as oxidant to see if this selectivity could be improved. Molybdenum sulfide had very little activity at 450–550°C. No furan, thiophene, or other four-carbon compounds were formed; the main products were carbon monoxide and propylene. Fresh iron-calcium phosphate gave complete combustion to CO<sub>2</sub>, presumably due to oxygen on the catalyst. The catalyst was still active after sulfiding, giving mainly oxides and and sulfides of carbon, very little propylene and no evidence of four-carbon compounds.

*Mesityl oxide*

The oxidative cyclization of mesityl oxide to 2,4-dimethylfuran proceeds with good selectivity with oxygen over bismuth molybdate (10, 11) (77% selectivity at 37% conversion or 61% selectivity at 61% conversion). The sulfur dioxide oxidation of mesityl oxide was examined to see if this selectivity could be improved and also to ascertain to what extent sulfur enters the molecule instead of oxygen. Results with molybdenum sulfide catalyst are given in Table 7. Very little dimethylthiophene was formed: the selectivity to this material was only 1–2% at 500–600°C. Dimethylfuran was the major product formed with 79% selectivity at 47% conversion at 550°C. Other products were oxides and sulfides of carbon.

The use of sulfur dioxide instead of oxygen results in a selectivity increase of about 5%. A disadvantage of the sulfur dioxide system is that the catalyst requires periodic air regeneration.

## DISCUSSION

A brief summary of results for the various paraffins and olefins is given in Table 8. Reaction rates and product selectivities are very dependent on hydrocarbon feed structure. Branching and increasing chain length increase reactivity substantially. Dehydrogenation appears to be the first reaction in all cases. Olefins are dehydrogenated selectively to dienes, but at high conversions these dienes are converted to thiophenes. If there is a linear C<sub>4</sub> or C<sub>5</sub> chain, thiophenes are produced so fast that it is difficult to obtain large yields of olefin or diene intermediate from paraffins. If there is a C<sub>6</sub> or longer chain, aromatization becomes very rapid and thiophene formation is quite low. Cyclic C<sub>5</sub> rings go to coke. Certain reactions stand out as interesting: olefins to dienes, dienes to thiophenes, cyclization of mesityl oxide, isobutane to isobutylene, butane and isopentane to the corresponding thiophenes, hexane to benzene, and 3-methylpentane to vinylthiophene. Certain surprises also occurred: very poor selectivity for propane to propylene presumably due to low propane reactivity, large amount of dealkylation and combustion for 2-methylpentane, and large amounts of coke and toluene from 3-ethyl-1-pentene.

Catalytic oxidation with sulfur dioxide

TABLE 7  
OXIDATION OF MESTITYL OXIDE WITH SULFUR DIOXIDE; MOLYBDENUM SULFIDE CATALYST

Time (min)	Pressure (atm)		GHSV	Temp. (°C)	C <sub>8</sub> H <sub>10</sub> O conv. (%)	Selectivity (%)		
	C <sub>8</sub> H <sub>10</sub> O	SO <sub>2</sub>				C <sub>8</sub> H <sub>10</sub> O	C <sub>8</sub> H <sub>8</sub> S	CS <sub>2</sub> + COS + CO <sub>2</sub> + CO
15	0.14	0.43	650	450°	22	62	10	28
30	0.17	0.42	220	450°	45	60	6	35
45	0.17	0.33	550	500°	51	68	2	29
60	0.19	0.27	680	550°	30	79	1	19
75	0.20	0.20	230	550°	47	79	1	20
90	0.25	0	180	550°	18	82	2	17
105	0.15	0.43	430	600°	58	66	1	32
120	0.19	0.27	680	600°	22	73	1	26
135	0.19	0.27	680	550°	4	70	1	28

TABLE 8  
SUMMARY OF PARAFFIN AND OLEFIN OXIDATION WITH SULFUR DIOXIDE

Compound	Results and remarks
Isoamylene	Fast and selective to diene: 80% S at 40% C; methylthiophene formed sequentially from diene.
Butylene	Fast and selective to diene: 85% S at 40% C; thiophene formed sequentially from diene.
Propylene	Moderately slow and unselective. Mainly combustion products.
Propane	Very slow, very poor selectivity to propylene (11% C, 54% S; 16% C, 30% S).
<i>n</i> -Butane	Moderately slow, forms unsaturates but rapidly cyclizes to thiophene, best C <sub>4</sub> H <sub>8</sub> + C <sub>4</sub> H <sub>6</sub> : 48% S at 52% C, best thiophene: 64% S at 71% C.
Isobutane	Moderate rate to isobutylene: 70% S at 26% C, 61% S at 50% C.
Isobutylene	Practically no reaction, only combustion products.
Isopentane	Moderately fast, at 48% C: 61% S to methylthiophene, 12% S to isoamylene, and 16% S to isoprene.
<i>n</i> -Hexane	Moderately fast, at 68% C: 74% S to benzene, 14% S to linear unsaturates.
Methylcyclopentane	Moderate rate to coke.
2-Methylpentane	Moderately fast, low selectivity to unsaturates and dimethylthiophene, surprisingly large amounts of dealkylation and combustion.
3-Methylpentane	Fast, >40% S to vinylthiophene at 40–60% C.
3-Methyl-1-pentene	Fast to diene, 37% S to vinylthiophene at 95% C, appreciable amounts of dimethylthiophene.
3-Ethyl-1-pentene	Large amounts of coke and about 30% S to toluene, methylethyl and methylvinylthiophene low.
<i>n</i> -Dodecane	Fast, very little thiophene or combustion, at 36% C: 31% S to olefins, 13% S to diolefins, 29% S to aromatics and 28% to cracked products.

certainly holds promise for certain reactions but the behavior of various hydrocarbons is quite dependent on individual structure.

The nature of the catalyst surface is not known, but in a number of cases it would appear to be predominantly in the sulfide form. The oxygen that is in the sulfur dioxide ends up in the form of water and may go through a surface oxide stage. The increased selectivity of isoamylene oxidation over sulfided bismuth molybdate with sulfur dioxide instead of oxygen is clearly due to a chemical modification of the surface, because an oxide surface will give large amounts of carbon dioxide and other oxygenated compounds even when sulfur dioxide is fed. The coke buildup and lower activity of the sulfide catalysts are also significant.

It is not at all clear how these catalysts work. Metal phosphates and sulfides are generally good for oxidation with sulfur dioxide, with the phosphates being preferred since they do not have a tendency to absorb excess oxygen, which leads to combustion. The reaction is clearly an oxidation intimately

involving the sulfur dioxide, since reaction of the hydrocarbon essentially ceases when the sulfur dioxide is removed from the feed. Thus the reaction is not a simple dehydrogenation followed by reaction of the hydrogen produced with the sulfur dioxide to give hydrogen sulfide and water. The reactions appear to start with relatively simple hydrogen atom abstractions. It is not known whether this abstraction is done by the catalyst or by an adsorbed species formed from the sulfur dioxide in analogy with the bismuth molybdate–oxygen system where the hydrogen atom abstractions are performed by adsorbed oxygen atoms (2).

For many feeds, the sulfur dioxide oxidation system offers substantial selectivity advantages over the oxygen system. This is due mainly to a much lower susceptibility to combustion and a lack of direct incorporation of heteroatoms in the feed molecule.

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