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Exploratory Catalytic Oxidations with Bismuth Molybdate

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Exploratory oxidations of various hydrocarbons and other compounds over bismuth molybdate (Bi:Mo = 1) are described. Bismuth molybdate is a very good dehydration catalyst for methyl vinyl carbinol and crotyl alcohol. Only the oxidized form of the catalyst is active. In contrast, isopropyl alcohol is dehydrated by both the oxidized and reduced forms. Bismuth molybdate is also a fairly good catalyst for oxidative dehydrocyclization; mesityl oxide is converted into 2,4-dimethylfuran quite well, while crotonaldehyde is converted into furan with less selectivity. The oxidation of alkyl aromatics is not particularly selective, due to dealkylation and complete combustion. Monochloropropenes are oxidized to nonchlorinated acrolein, but the hydrogen chloride formed rapidly attacks and destroys the catalyst.

INTRODUCTION

Bismuth molybdate has been shown to be an excellent catalyst for the oxidation of propylene to acrolein (*1*) and, in the presence of ammonia, to acrylonitrile (*2*) and for butylene to butadiene (*3*). The reactions of a large number of olefins have been reported (*4*). Butadiene is oxidized to furan, while hydrogen and paraffins such as *n*-butane and isobutane are inert (*5*). The present report summarizes results of oxidizing a variety of other materials with this interesting oxidation catalyst. In many cases, conditions were varied widely in a search for optimum results.

The catalysts used here were unsupported bismuth molybdates, 10–20 mesh, having preparations similar to those given in ref. (*5*). They were precipitated from an ammonium molybdate solution by mixing with acidified bismuth nitrate with addition of aqueous ammonia to give a final slurry pH of 5. After washing with water and drying at 120°C, the catalysts were calcined in air at 500°C for 2 hr. The atomic ratio of bismuth to molybdenum was unity. No X-ray determinations of the crystalline phases present were made. All reactions were carried out in glass or quartz reactors using about 2 cc of catalyst. The feed gas usually consisted of about 20% by volume of the vapor of the material to be oxidized and 80% of an artificial air made up of 20% O_2–80% He. The gaseous effluent was sampled immediately below the reactor through a small continuous leak to a mass spectrometer. The pressure in the reactor was atmospheric and conditions were usually held constant for about 15 min, analysis being taken during the last 5 min, after which the temperature and flow rate would be adjusted to another set of conditions. The data are calculated on the basis of the gaseous products, assuming no losses, and the selectivity refers to the number of carbon atoms in the given product compared to the number of carbon atoms in the feed converted. Conversion is the amount of feed converted to all products. GHSV refers to volume of total feed gases at 25°C and 1 atm/hr per bulk volume of catalyst.

RESULTS AND DISCUSSION

Ethylene–Nitric Oxide–Propylene Mixtures

The proposed mechanism of olefin oxidation over bismuth molybdate (*6*) would indicate ethylene to be inactive, since it has no weak allylic hydrogen. This is indeed the case; this olefin is essentially inert. At a very low flow rate (total GHSV = 225 with $C_2H_4/O_2 = 2$) at 500°C, the ethylene conversion was 29%. The only carbon products detected were CO_2 (70%) and CO (30%).

Although ethylene is oxidized very slowly, it might interfere or interact with propylene oxidation. Therefore, mixtures of ethylene and propylene were oxidized; the results are shown in Table 1. There was very little conversion of the ethylene, too low for the analytical system to pick up the difference. The results in the table have been calculated assuming no ethylene conversion. There is no significant effect of ethylene on the propylene conversion; but the amount of acetaldehyde formed, particularly at the lower temperatures, is greater with the ethylene present. It is difficult to estimate whether this is a result of the direct oxidation of the ethylene or an influence of the by-products from propylene. Whatever may be the cause of these differences at lower temperature, the presence of ethylene has essentially no effect on the oxidation of propylene over this catalyst under optimum conditions for the production of acrolein.

TABLE 1

OXIDATION OF ETHYLENE–PROPYLENE MIXTURES[a]

Temperature (°C):	420°		460°		480°	
C_2H_4 present:	Yes	No	Yes	No	Yes	No
Conversion[b] (%)						
O_2	36	47	67	75	77	95
C_3H_6	42	38	64	62	74	75
Selectivity[b] (%)						
Acrolein	70	82	74	81	79	81
Acetaldehyde	16	6	12	7	7	5
Other	14	12	14	12	14	14

[a] GHSV = 5760; atmospheric pressure; 10% O_2, 10% C_3H_6, 20% H_2O, 20% C_2H_4 or added Ar, 40% Ar.

[b] Calculated assuming no reaction of the ethylene.

There is a possibility in the oxidation of propylene to acrolein that gas-phase free radical reactions occur, either in the main reaction after initiation on the surface or in the side reactions that produce mainly CO_2 (*7, 8*). It was thought possible that nitric oxide, a stable free radical, would affect these reactions. Various amounts of NO were added to a feed mixture of propylene, oxygen, and argon and passed over a catalyst at 460°C. The ratio of NO to O_2 was varied from 0.05 to 2.0. No effect was noted on the relative amounts of CO_2 produced and only a very small suppressive effect on the overall rate. The main product was acrolein, with or without NO. The overall rate was reduced no more than 20% at the highest concentrations of NO used and small amounts had no detectable effect. The NO appeared to pass through the reactor unchanged. No acrylonitrile was detected. We conclude that either no gas-phase reactions occur or that nitric oxide does not alter their kinetics significantly. It must be remembered that oxygen itself is biradical and another free radical like NO might have little additional effect when oxygen is present.

Chloropropenes

The monochlorinated propylenes were investigated for production of chlorinated oxidation products and to look for any anomalies in the oxidation process due to the easily removable and reactive chlorine atoms.

In the oxidation of allyl chloride, acrolein was produced very selectively, giving over 90% selectivity at 75% conversion at 425°C and 1500 GHSV. No significant amount of oxygenated chlorine-containing material was found. However, the catalyst dropped markedly in activity and selectivity within a few minutes and copious amounts of brownish-black material deposited in the lines below the reactor. This material was probably volatile molybdenum chloride formed by attack on the catalyst by hydrogen chloride.

The chlorine in allyl chloride is quite reactive, while that in 2-chloropropene is much less so. Therefore, retention of chlorine in the oxidation product would be much more likely for the latter compound. 2-Chloropropene and helium-oxygen were passed over a catalyst at a total GHSV of about 3500 and temperatures of 340° and 430°C. Initially, the major product was acrolein with no evidence of chlorine-containing oxidation products, not even hydrogen chloride, in the exit stream. No substantial amounts of CO_2 were found at any time. However, rather quickly, other reaction products began to appear, including propylene and acetaldehyde. When ammonia was added, the acrolein and acetaldehyde were converted to the corresponding nitriles, with a very mild lowering in rate of oxidation of the chloropropene. After a few more minutes, the gas flow slowed due to plugging, and examination showed heavy brownish-black deposits below the reactor zone, probably volatile metal chlorides. The oxidation of chlorine-containing compounds presents two formidable problems: the retention of chlorine in the molecule and the prevention of destruction of the catalyst by chlorine by-products, especially hydrogen chloride.

Alkyl Aromatics

It has been shown elsewhere (*4*) that the bismuth molybdate system operates by breaking the fairly weak allylic C–H bond. The methyl C–H bond in toluene is very similar in character and strength to the allylic bond in olefins. Therefore, benzaldehyde should be made quite readily from toluene. Only one run was made with toluene over bismuth molybdate at 460°C and GHSV = 2100. Toluene conversion was 74% and the selectivity to benzaldehyde was only 18%. Selectivity to benzene was 22% and to CO_2 and CO was 43% and 18%, respectively. These quite poor results might be improved under different conditions, but clearly difficulties will be encountered with dealkylation and combustion.

Ethylbenzene was oxidized at two temperatures. At 420°C and GHSV = 1000, the conversion of ethylbenzene was 70% and the selectivity to styrene was 19%. Selectivities to benzaldehyde, benzene, CO_2, and CO were 14%, 14%, 34%, and 19%, respectively. At 490°C and GHSV = 4200, the conversion was 64% and selectivity to styrene was 30%, while that to benzaldehyde, benzene, CO_2, and CO was 23%, 9%, 27%, and 12%. It would appear that ethylbenzene is oxidized to styrene, but that the styrene formed is degraded too rapidly to permit good yields of styrene in the final product.

Styrene was oxidized at GHSV = 2400. There was a large hot spot in the reactor and the temperature ranged from 270° to better than 500°C, with the average about 450°C. The styrene conversion was 46%, with a selectivity to benzaldehyde of 43%. Selectivities to benzene, CO_2, and CO were 17%, 35%, and 4%.

α-Methylstyrene can be considered as either a substituted aromatic or a substituted propylene. Substituted aromatics give benzaldehyde, benzene, and CO_2 as principal products while substituted propylenes give substituted acroleins. A mixture of α-methylstyrene and air was fed over bismuth molybdate under various conditions of temperature and gas compositions. The reaction was fast and in all cases limited by one or the other of the reactants. At 494°C, total GHSV of 2200, and hydrocarbon-to-oxygen molar ratio of 1:4, the conversion of α-methylstyrene was 45%. The carbon selectivity to various products was as follows: phenylacrolein, 7%; benzaldehyde, 25%; benzene, 27%; CO_2, 36%; CO, 6%. Even less phenylacrolein was made under other conditions. In air oxidation over bismuth molybdate, α-methylstyrene thus behaves as a substituted aromatic rather than as a substituted propylene.

Methyl Ethyl Ketone

Due to conjugation with the carbonyl group, the secondary C–H bonds in methyl ethyl ketone (MEK) should be weakened, and it might be possible to form methyl vinyl ketone (MVK). The air oxidation of methyl ethyl ketone was investigated with the following results being obtained at 450°C, O_2/feed molar ration ~ 3, GHSV ~ 3500, and atmospheric pressure.

MEK conversion: 31%	
Selectivity:	
Methyl vinyl ketone	21%
$m/q \sim 86$ (prob $C_4H_6O_2$)	~10%
CO_2	37%
CO	28%
CH_4	4%

A small amount of acrylic acid may have been made, but it was undetected since its mass spectrum is very difficult to unravel from that of MEK and MVK. Selectivity results at 380°C were little different from these. Methyl ethyl ketone may at first be oxidized to methyl vinyl ketone, but as the results below show, the latter is rapidly oxidized further.

Methyl vinyl ketone was oxidized at 450°C, O_2/feed ratio ~ 3, and GHSV ~ 3500.

MVK conversion: 48%

Selectivity:

Acrylic acid	~ 32%
CO_2	34%
CO	30%
CH_4	3%

The reproducibility for acrylic acid was quite poor. Methyl vinyl ketone is oxidized quite rapidly, mainly to complete combustion.

Alcohols

Several alcohols have been oxidized over bismuth molybdate, with some interesting results.

Allyl alcohol was oxidized at 450°C, GHSV = 3400, $C_3H_5OH/O_2 = 0.7$, with the following results: allyl alcohol conversion, 95%; selectivity to acrolein, 85%. A comparison of these data with those of propylene oxidation shows that allyl alcohol is oxidized to acrolein much faster and more selectively than propylene. In the absence of tagging experiments, it is not clear whether allyl alcohol is oxidized by dissociation of the hydroxyl with subsequent oxidation of the symmetrical allyl radical, or rather by oxidation of the carbinol group with retention of the carbon and oxygen identity. The very rapid dehydrations discussed below indicate that the first mechanism is at least feasible.

Crotyl alcohol was oxidized at 450°C. The results are shown in Table 2. Under these same conditions, with sufficient oxygen for reaction, butene-2 would give about 20% conversion while butene-1 would give about 45%.

Crotyl alcohol forms butadiene over bismuth molybdate quite selectively and at a rate much faster than the oxidation of the corresponding olefin. The startling result is that this dehydration reaction requires at least traces of oxygen with the catalyst. It would appear that only the oxidized form of the catalyst is active. Ammonia inhibits the reaction, although no nitrogen-containing organic compounds were detected. The amount of crotonaldehyde found in these experiments is substantially higher than that found in the oxidation of the olefin. This may be due to a high concentration of crotyl alcohol in the feed. If crotyl alcohol is formed in the olefin oxidation, it is immediately dehy-

TABLE 2

REACTION OF CROTYL ALCOHOL OVER BISMUTH MOLYBDATE[a]

Oxygen (cc/min)	Ammonia (cc/min)	Crotyl alcohol conversion (%)	Selectivity (%)			
			Butadiene	Crotonaldehyde	Furan	CO_2
40	—	96	89	3	3	4
20	—	90	88	6	1	4
10	—	91	90	5	1	3
2.5	—	83	89	7	2	2
1	—	83	85	7	6	2
0	—	10	(~100)[b]	—[b]	—[b]	—[b]
40	10	67	72	16	4	8
40	40	24	58	16	16	10
0	40	20	86	5	5	5

[a] 450°C; 2 cc of catalyst; 220 cc/min of helium (STP), and 20 cc/min of gaseous crotyl alcohol.

[b] Not accurate.

TABLE 3
Reaction of Methyl Vinyl Carbinol over Bismuth Molybdate[a]

Partial pressure		MVC conversion (%)	Selectivity (%)				
O_2	NH_3		Butadiene	Furan	MVK	Acrylic acid	$CO + CO_2$
0.13	—	99	85	3	4	0.3	8
0.07	—	99	87	3	3	0.3	7
0.03	—	98	86	2	6	0.3	6
0.01	—	35	72	2	15	6	5
0.00	—	13	42	2	16	16	10
0.13	0.03	99	76	4	8	0.4	12
0.13	0.13	99	85	3	2	0.2	11
0.00	0.13	6	27	4	27	4	39

[a] 450°C, GHSV = 18,000, MVC partial pressure = 0.14 atm.

drated and its concentration is extremely low. Moreover, crotonaldehyde is oxidized into furan and CO_2 with this catalyst so that with the olefin oxidation lower amounts of crotonaldehyde would be expected.

Methyl vinyl carbinol, an isomer of crotyl alcohol, was reacted over another bismuth molybdate with the results shown in Table 3. Methyl vinyl carbinol produces butadiene very selectively and the reaction stops when no gaseous oxygen is fed, in analogy with crotyl alcohol. However, in contrast, methyl vinyl carbinol is not inhibited by ammonia. Data are given in Table 4 for the oxidation of methyl vinyl carbinol at lower temperatures, where the selectivity to butadiene is somewhat less due to formation of methyl vinyl ketone. The data of Table 4 indicates roughly that the reaction is first order in alcohol and the calculated apparent activation energy is about 20 kcal/mole. Taking the ratio of

TABLE 4
Oxidation of Methyl Vinyl Carbinol over Bismuth Molybdate[a]

Temp. (°C)	GHSV	P_{O_2}	MVC conv. (%)	Selectivity (%)				
				Butadiene	Furan	MVK	Acrylic acid	$CO + CO_2$
281°	5 500	0.22	33	70	0.6	20	7	3
302°	5 500	0.22	38	71	0.5	19	7	3
327°	5 500	0.22	58	75	0.6	18	4	3
361°	5 500	0.22	85	79	0.5	16	1	3
394°	5 500	0.22	96	78	0.5	15	0.7	6
319°	33 400	0.14	20	68	0.5	15	9	7
329°	33 400	0.14	15	62	0.8	17	9	11
344°	33 400	0.14	19	67	0.6	18	7	8
322°	16 700	0.14	11	65	0.0	18	6	10
341°	16 700	0.14	20	71	0.5	17	6	5
363°	16 700	0.14	35	74	0.5	16	4	5
379°	16 700	0.14	42	75	0.4	17	3	4
376°	16 700	0.07	32	72	0.5	19	4	4
379°	16 700	0.03	24	74	0.3	19	4	3
373°	16 700	0.00	5	76	—	19	5	—
381°	16 700	0.004	16	71	0	17	4	8
381°	16 700	0.002	13	73	0	19	3	5
380°	16 700	0.002	11	70	0	19	3	8
380°	16 700	0.002	10	72	0	20	3	4

[a] Partial pressure of C_4H_8O = 0.12.

TABLE 5

Reaction of Isopropyl Alcohol over Bismuth Molybdate[a]

Oxygen in feed (%):	2	2	2	2	0	4	9	9	9	9
Temperature (°C):	385°	416°	480°	385°	375°	378°	378°	220°	235°	250°
Time (min):	10	30	50	70	90	105	120[b]	230	250	265
IPA conversion (%)	99	96	100	80	99	100	100	48	57	69
Selectivity (%)										
Propylene	88	81	90	67	90	95	96	63	77	80
Acetone	11	17	6	28	8	4	3	17	15	15

GHSV = 15 000; IPA in feed = 9% molar.

[b] He over catalyst for 95 min.

catalyst activities (MVC catalyst/CA catalyst) = 3.54 as determined elsewhere by propylene oxidation, the rate of reaction of methyl vinyl carbinol is about the same as that of crotyl alcohol.

It has been shown previously (*9*) that isopropyl alcohol (IPA) is dehydrated rapidly over bismuth molybdate catalyst. In view of the somewhat unusual results of the dehydration of crotyl alcohol over bismuth molybdate, where oxygen was required for activity, the dehydration of isopropyl alcohol was examined more closely. (See Table 5.) No acrolein was detected, since the dehydration of isopropyl alcohol is several tens of times faster than the oxidation of propylene. A small amount of acetone was found. This amount appeared to decrease with increasing temperature, although some variation with time was also found. The dehydration of isopropyl alcohol over bismuth molybdate is a very fast reaction and is faster than that of crotyl alcohol. It apparently is not affected by the absence of oxygen, in contrast to crotyl alcohol. It would appear that the mechanism is different from that of the allylic alcohol, probably involving direct attack of the secondary hydroxyl group.

It has been shown above that isopropyl alcohol dehydrates very rapidly to propylene, while normal saturated alcohols react more slowly, but give no major products, degradation to a variety of products occurring as well as some complete oxidation (*9*). It would then be predicted that 1,3-butanediol would react rapidly and selectively to give butadiene, by way of crotyl alcohol. It does react rapidly (85% conversion with complete conversion of oxygen at 408°C and GHSV = 5400) but gives only about 10–15% selectivity to butadiene and to crotyl alcohol, with similar amounts of methyl vinyl ketone, propionaldehyde or acetone, acrolein, acetaldehyde, formaldehyde, CO_2, etc., being formed. Temperature variation of 390–490°C did not alter the picture. Reaction to this conglomeration of products even occurred for a short time after gaseous oxygen was stopped in the feed. 1,3-Butanediol reacts like the normal saturated alcohols rather than like isopropyl alcohol.

Cyclization to Furans

Certain unsaturated carbonyl compounds are cyclized to furans. Crotonaldehyde is oxidized to furan with only fair selectivity, the other products being CO and CO_2. No evidence for the dialdehyde was found. The reaction is quite rapid, much faster than that expected for oxidation of the methyl group to aldehyde. Data are given in Table 6. The best results obtained were at 420°C: 47% selectivity at 93% conversion. In-

TABLE 6

Oxidation of Crotonaldehyde[a]

Temperature (°C)	GHSV	C_4H_6O conversion (%)	Furan[b] selectivity (%)
350°	1600	56	29
390°	5400	68[c]	32
420°	1600	93[c]	47
500°	5100[d]	64[c]	14

[a] Partial pressure C_4H_6O = 0.17 = partial pressure O_2.

[b] Rest is CO + CO_2.

[c] 100% O_2 conversion.

[d] P_{O_2} = 0.10.

TABLE 7
Oxidation of Mesityl Oxide over Bismuth Molybdate

Temperature (°C)	GHSV	Partial pressure (atm) Mesityl oxide	Partial pressure (atm) O_2	Conversion (%) Mesityl oxide	Selectivity (%) Dimethylfuran
400°	1,300	0.18	0.12	60	15
420°	1,280	0.18	0.12	73	19
450°	18,900	0.17	0.13	73	59
500°	18,900	0.17	0.13	37	77
500°	13,400	0.16	0.18	61	61

creasing temperature appeared to reduce selectivity.

Bismuth molybdate is a good catalyst for oxidative dehydrocyclization of mesityl oxide to 2,4-dimethylfuran (*10*). A survey of operating conditions (Table 7) gave the best results at 500°C: 77% selectivity at 37% conversion or 61% selectivity at 61% conversion. Lower temperatures gave lower selectivity.

Isomesityl oxide, 2-methyl-1-pentene-4-one, was oxidized with bismuth molybdate over the temperature range 350–500°C. Selectivity to dimethylfuran was substantially less than with mesityl oxide. At 440°C and 41% conversion, selectivities to dimethylfuran, methyl furfural, and carbon oxides were 47%, 6%, and 47%, respectively.

Conclusions

Bismuth molybdate, previously shown to be a good catalyst for olefin oxidation, is also a very good catalyst for dehydrating certain unsaturated alcohols. Only the oxidized form of the catalyst is active. It is also a very active catalyst for the dehydration of isopropyl alcohol, even in the absence of oxygen. The pattern of dehydration activity is not easy to discern; some systems are sensitive to ammonia and others are not, and extensions to alcohols of more complicated structure do not give the predicted results.

Bismuth molybdate is also a good catalyst for the cyclization of mesityl oxide to 2,4-dimethylfuran, but the conversion of crotonaldehyde to furan is less selective.

Retention of chlorine in the oxidation of monochloropropenes does not occur and the catalyst is destroyed by the chloride released.

The oxidation of alkyl aromatics is not nearly so selectives as the corresponding olefins; dealkylation and combustions are prominent reactions.

In summary, bismuth molybdate, although active and selective for a variety of reactions, is not a universal oxidation catalyst and various subtleties of the oxidation system have a profound bearing on the results. Much still remains to be learned before the behavior of this oxidation catalyst is completely understood.

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