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The Catalytic Oxidation of 1-Butene over Bismuth Molybdate Catalysts

V. The Kinetics of the Oxidation: A. Pulse Reaction Kinetics; Exploratory Experiments for a Kinetic Investigation

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The kinetics of oxidation of 1-butene with oxygen on three types of bismuth molybdate catalysts were investigated in pulse experiments. For all the catalysts mentioned the kinetics can be expressed by a first-order dependency on the butene pressure and a zero-order dependency on the oxygen pressure. A slight deviation in the kinetics was observed for the Bi/Mo = 2/1 catalyst, attributed to diene inhibition but not important enough to affect the kinetics. Low activation energies in the order of 10–11 kcal mole^{-1} were found for all the catalysts over a wide range of temperatures. A high activation energy of 33 kcal mole^{-1} was found with the Bi/Mo = 2/1 catalyst at low temperatures when butadiene was admixed to the pulses of 1-butene and oxygen. A confirmation of the reduction–reoxidation mechanism, earlier proposed by us, was obtained with the pulse technique.

INTRODUCTION

In a previous paper (*1*), we reported on a new method of preparation of various Bi/Mo catalysts with different compositions and activities for the oxidation of butene. The highest activity was observed for the Bi/Mo = 2/1 catalyst, low-temperature koechlinite, which had been calcined at 500°C for 2 hr. Another good active phase was the Bi/Mo = 1/1 catalyst, calcined at 600°C for 1 hr, of which the X-ray diagram was similar to that published by Erman *et al.* (*2*). The Bi/Mo = 2/3 catalyst, calcined at 500°C for 2 hr, was found somewhat less active. The Bi/Mo = 2/1, 680°C catalyst, the high temperature modification reported by Blasse (*3*), was found far less active, possibly because of a lower surface area. In the rate measurements, in which we assumed first order kinetics for butene and zero-order dependency on oxygen, particularly the Bi/Mo = 2/1, 500°C catalyst showed a remarkable change in the activation energy as function of reciprocal temperature. The present paper deals primarily with a detailed investigation into the kinetics and the change in activation energy of the Bi/Mo = 2/1, 500°C catalyst. The kinetics for the other catalysts are also investigated, be it in somewhat less detail. The kinetics of the oxidative dehydrogenation of butene to butadiene reported below are derived from pulse experiments in microreactor systems. In the following papers we shall report on different types of experimental techniques.

EXPERIMENTAL PROCEDURE

The pulse apparatus is simple of construction. The microreactor, placed in a furnace (an electrically heated Al block), is connected on the entrance side to switch cocks, while the exit is connected to a gas chromatographic column. A constant flow of helium of 40 cm^3 min^{-1}, the carrier gas, first passes the switch cocks, then is passed

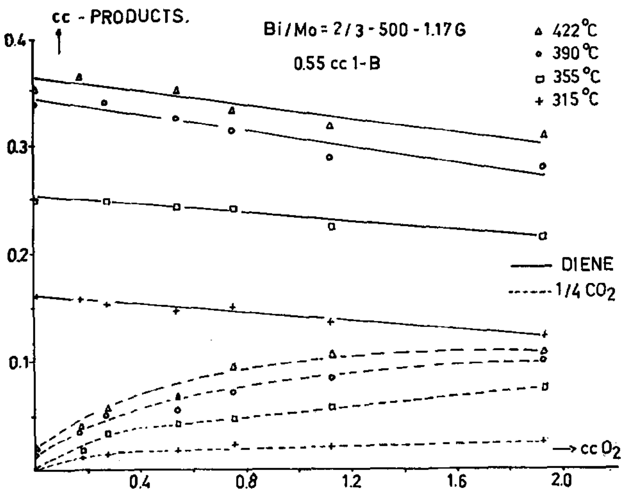

FIG. 1. Butadiene and CO_2 formation (ml) in the oxidation of 0.55 ml of 1-butene with varying amounts of oxygen on 1.17 g of Bi/Mo = 2/3 catalyst at different temperatures.

over 1170 mg of catalyst (particle size 0.10–0.20 mm) in the microreactor and finally enters the 4-m column filled with 20% dimethylsulfolane (by wt) on chromosorb. Two switch cocks, placed very close to each other, were used: One for connection with a sample loop for oxygen, the other for a loop with 1-butene. The cocks are switched simultaneously and with use of conductivity detection it was checked that

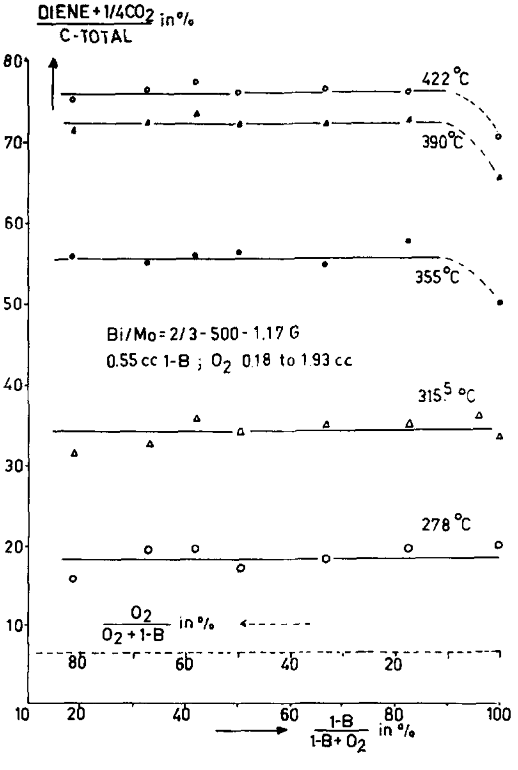

FIG. 2. Determination of the oxygen-order dependency on the Bi/Mo = 2/3 catalyst at different temperatures with a constant amount of 1-butene and varying amounts of oxygen.

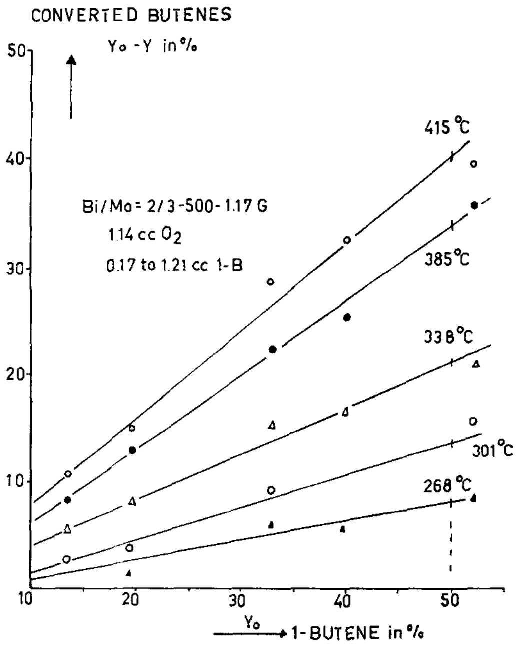

FIG. 3. Determination of the butene-order dependency on the Bi/Mo = 2/3 catalyst at different temperatures with a constant amount of oxygen and varying amounts of 1-butene.

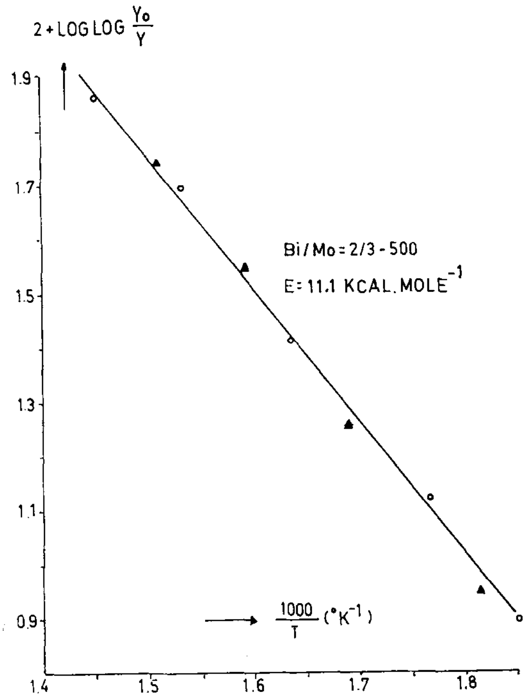

FIG. 4. Arrhenius plots according to a first-order dependency on 1-butene and a zero-order dependency on oxygen: ▲, data calculated from Fig. 2 with $Y_0 = 100$ (method 1); ○, data calculated from Fig. 3 with $Y_0 = 50$ (method 2).

oxygen and butene were mixed before they entered the catalyst zone. The volume of a pulse (or loop) of one component can be kept constant while that of the other can be varied by use of loops of different volumes. The obvious disadvantage of this procedure is that the total amount of reactants is not constant. The alternative is to work with one cock with one loop as the pulse system. This requires that the loop be filled by adjustment of butene and oxygen flows. The total amount of reactants is then constant, but we found the flows to be dependent on each other which means that it is difficult to maintain one of the flows constant while that of the other is varied. Nevertheless, both systems were applied by us in the experimental procedure and the results were similar. Note that in all our experiments the catalyst was kept in the highest state of oxidation: the catalyst, before and after reaction, was treated with a pulse of pure oxygen.

ANALYSIS AND CALCULATIONS

The following compounds are detected and recorded: oxygen, CO_2, 1-butene, *trans*-2-butene, *cis*-2-butene, and butadiene. We neglected the production of possibly undetected but invariably small amounts of other oxygenated products. The signals recorded have to be corrected by sensitivity factors for comparison of the gaseous compounds in units of volume. These multiplying factors are: CO_2 (1.8×), O_2 (2.0×), butadiene (1.03×). Steam is not recorded, because it is condensed in front of the column, but the amount was calculated from summation of the corrected values of CO_2 and butadiene.

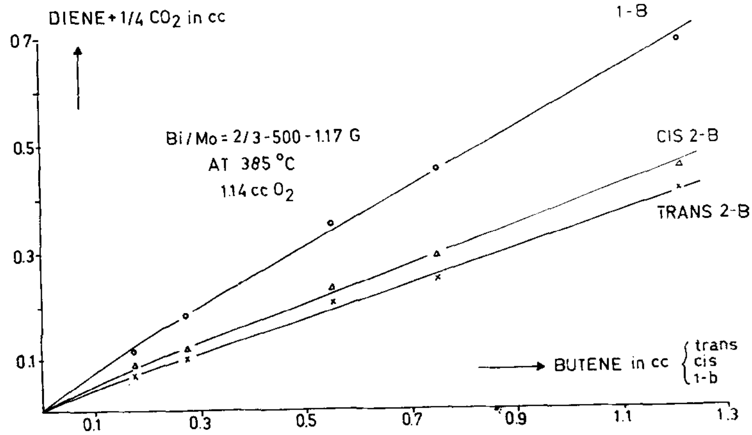

FIG. 5. Comparison of the oxidation activities of *trans*-2-butene, *cis*-2-butene, and 1-butene on the Bi/Mo = 2/3 catalyst at 385°C.

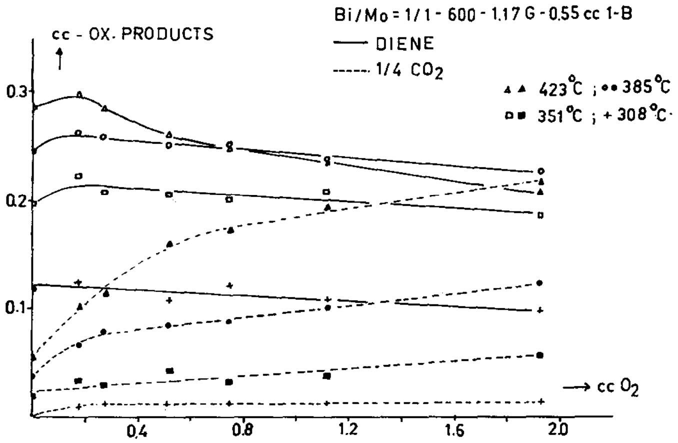

FIG. 6. Butadiene and CO_2 formation (ml) in the oxidation of 0.55 ml of 1-butene with varying amounts of oxygen on 1.17 g of Bi/Mo = 1/1 catalyst at different temperatures.

Two methods were used to convert the data into a form suitable for expressing the kinetics: (i) a simple but approximate one, based on calculations in which only the carbon-containing compounds are considered and in which oxygen and steam are neglected. This method is justified by the observation that during reaction the disappearance of oxygen is equivalent to the production of water. This method appeared to be correct as long as the CO_2 production remained small. (ii) An accurate method consists of calculations in which all actual partial concentrations (including those of O_2 and steam) are used.

With the first method the butene concentration before reaction is taken 100% and with high production of oxidated compounds one can reach conversion values near to it. In the second method the butene concentration is dependent on the amount of oxygen present and is expressed by the ratio 1-butene/(O_2 + 1-butene)·100% which usually is varying in the range between 10 and 50%. Now the conversion values never can exceed this 50%. The dif-

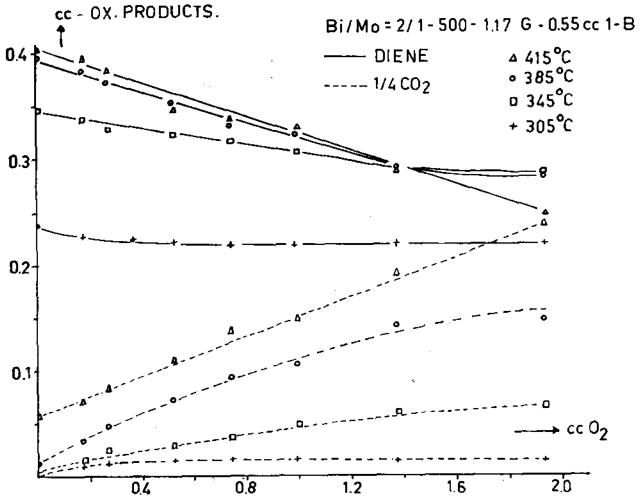

FIG. 7. Butadiene and CO_2 formation (ml) in the oxidation of 0.55 ml of 1-butene with varying amounts of oxygen on 1.17 g of Bi/Mo = 2/1 catalyst at different temperatures.

TABLE 1

METHOD OF CALCULATIONS

Method 1. Carbon-containing compounds (%)

Temp. (°C)	$\frac{1}{4}CO_2$	1-Butene	*trans*	*cis*	Diene	$\frac{1}{4}CO_2$ + diene
—	—	100	—	—	—	—
301	2.0	60.4	9.3	10.9	17.4	19.4
338	5.0	37.0	13.1	13.2	31.7	36.7
385	13.3	21.5	10.1	8.4	46.7	60.0

Method 2. Gas composition (%)

Temp. (°C)	O_2	CO_2	1-Butene	*trans*	*cis*	Diene	Steam[a]	Y^b	$Y_0 - Y^b$
—	60.3	—	39.7	—	—	—	—	39.7	—
301	49.4	3.1	23.4	3.6	4.2	6.6	9.7	31.2	8.5
338	39.3	7.3	13.5	4.8	4.8	11.5	19.8	23.1	16.6
385	25.8	16.5	6.6	3.1	2.6	14.5	31.0	12.3	27.4

[a] Calculated.

[b] Y = butenes; and $Y_0 - Y$ = conversion.

ference of scale is illustrated in Table 1 in which the data of the same experiment are handled according the 2 methods mentioned.

RESULTS

A. The $Bi_2O_3 \cdot 3MoO_3$ catalyst, calcined at 500°C. Figure 1 shows the selectivity of the oxidation of 0.55 ml of 1-butene, with respect to butadiene and carbon dioxide formation, as function of reaction temperature and of oxygen input. The slight decrease in diene formation with increasing volumes of oxygen is connected with an increase of CO_2 formation of the same order of magnitude. The selectivity of this catalyst is reasonable, and therefore in the determination of the oxygen-order dependency we used Method 1 in which oxygen and steam values are neglected. The results are represented in Fig. 2, which shows that over a wide range of temperatures the oxidation to diene + $\frac{1}{4}CO_2$ is zero order with respect to oxygen. At low temperatures the formation of oxidation products is equal to that without oxygen being present. These observations are strong arguments for the correctness of the reduction–reoxidation mechanism. In the absence of oxygen a slight decrease in the production is observed at higher temperatures [see Fig. 2 (---)]. For the determination of the butene-order dependency, we used Method 2 in which oxygen and steam values are also considered. Now varying amounts of 1-butene

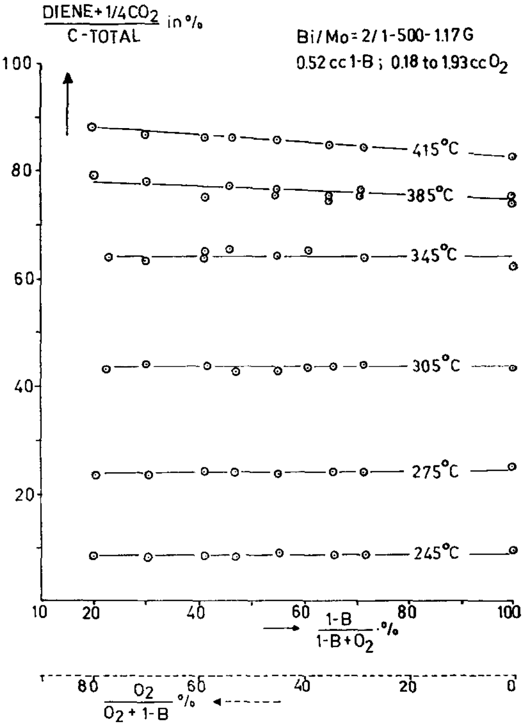

FIG. 8. Determination of the oxygen-order dependency on the Bi/Mo = 2/1 catalyst at different temperatures with a constant amount of 1-butene and varying amounts of oxygen.

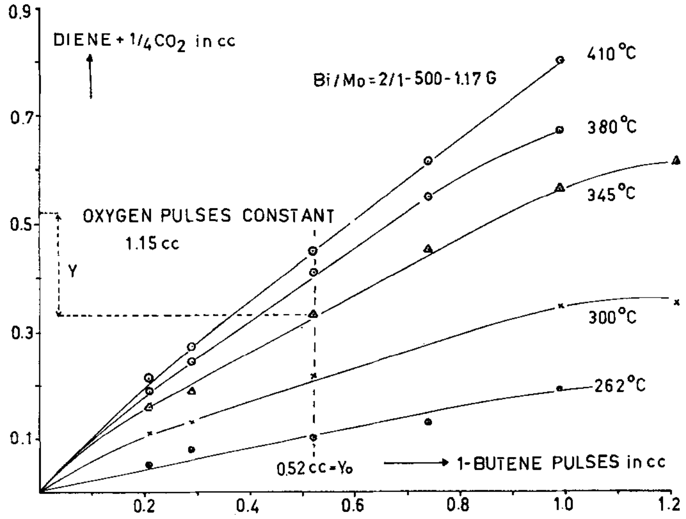

FIG. 9. Butadiene and CO_2 formation (ml) in the oxidation of varying amounts of 1-butene with a constant amount of oxygen on 1.17 g of Bi/Mo = 2/1 catalyst at different temperatures.

(from 0.17 to 1.21 ml) are oxidized with a constant volume of oxygen (1.14 ml) the latter remaining in excess with respect to the equimolar reaction. The amount of butenes converted are shown to increase linearly with the butene concentration (see Fig. 3) which points to a first-order dependency of 1-butene. Hence, according to these results, the reaction is zero order in oxygen and first order in 1-butene. From the data of ~ Figs. 2 and 3, the activation energy was calculated to be in the order of 11 kcal $mole^{-1}$. The data, represented in Fig. 4, are shown to fit a single line. The oxidative dehydrogenation activities of the butene isomers are represented in Fig. 5; and as shown, the sequence for increasing activities is: *trans*-2-butene:*cis*-2-butene: 1-butene = 0.57:0.63:1.0.

B. The $Bi_2O_3 \cdot 2MoO_3$ catalyst, the Erman phase. The results for this catalyst do not differ from those already mentioned for the $Bi_2O_3 \cdot 3MoO_3$ catalyst. Figure 6 for instance appears closely similar to Fig. 3 except for the fact that complete combustion is more pronounced. In view of this close similarity no further figures will be given. Again the reduction–reoxidation mechanism appears followed and the kinetics also can be expressed by a zero order on oxygen and a first order on butene. Even the activation energy of 10.5 kcal $mole^{-1}$ is equal within the experimental accuracy.

C. The $Bi_2O_3 \cdot MoO_3$ catalyst, low temperature koechlinite. Figure 7 shows that

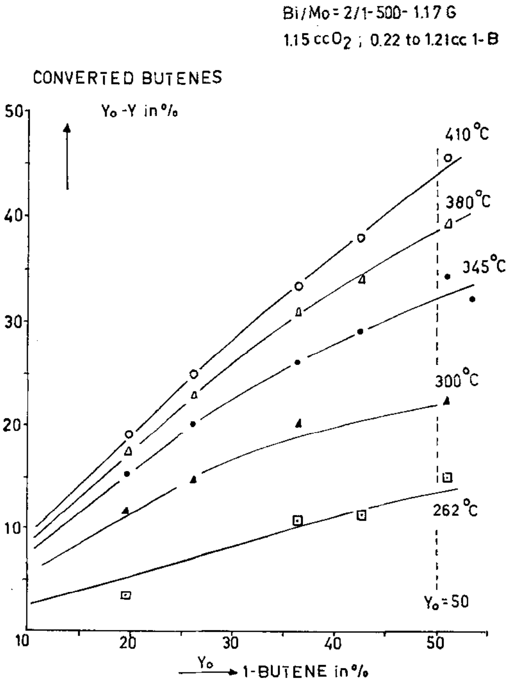

FIG. 10. The butene-order dependency calculated from the data of Fig. 9.

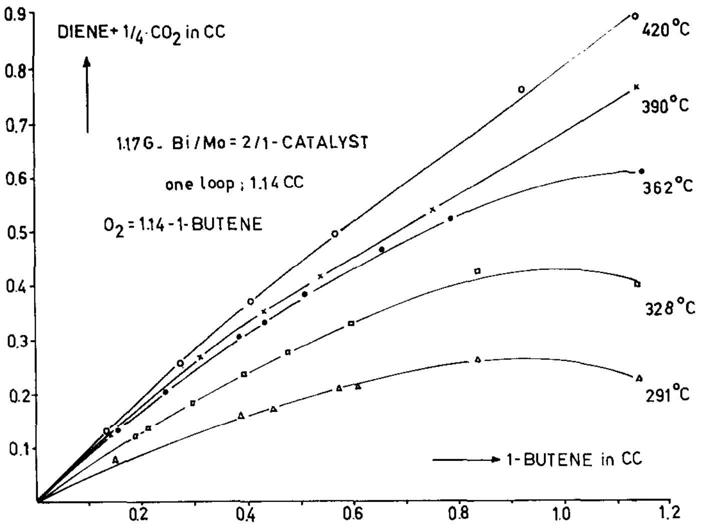

Fig. 11. Oxidation products (ml) as function of 1-butene (ml) added in the one-loop pulse system.

below a temperature of 385°C the selectivity of the catalyst is fairly good. At higher temperatures complete combustion is substantial. For determination of the oxygen-order dependency, Method 1 was used and the results are given in Fig. 8. A zero-order dependency of oxygen is present below 385°C; at higher temperatures a slight deviation is observed. Without oxygen, again, the formation of oxidation products is not decreased, in agreement with the reduction–reoxidation mechanism. For determination of the butene-order dependency, varying amounts of 1-butene (0.22–1.21 ml) ore oxidized with 1.15 ml of oxygen. The oxidation products (ml) are plotted against the 1-butene pulses (ml) and the results are represented in Fig. 9: as shown at the lower temperatures the lines are not linear. From these data and with use of Method 2 we obtained Fig. 10 in which the converted butenes are plotted against the 1-butene concentration of the input. Again, curved lines are observed from which the conclusion is drawn that a deviation in the first-order dependency of 1-butene occurs. To substantiate the similarity of the "one loop" and the "two loops" pulse methods, Fig. 11 gives the results for pulses in which the gas mixtures were made in one loop.

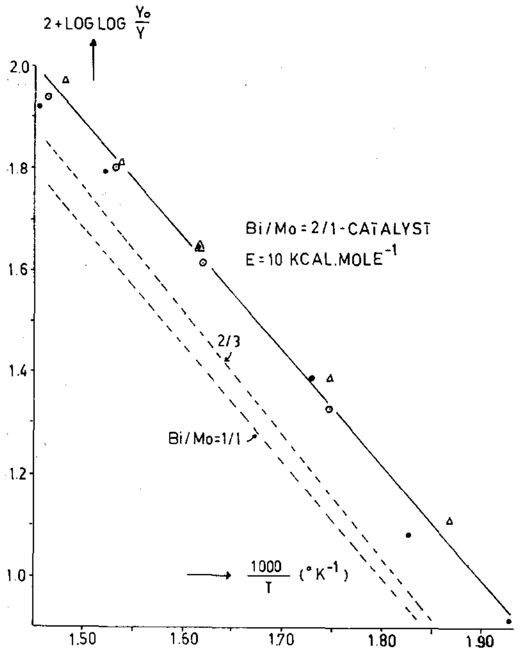

Fig. 12. Arrhenius plots according to a first-order dependency on 1-butene and a zero-order dependency on oxygen, of the Bi/Mo = 2/1 catalyst: ●, data calculated from Fig. 8 with $Y_0 = 100$ (Method 1); ⊙, data calculated from Fig. 9 with $Y_0 = 0.52$ ml (Method 1); △, data calculated from Fig. 10 with $Y_0 = 50$ (Method 2); - - -, the plots for the other catalysts.

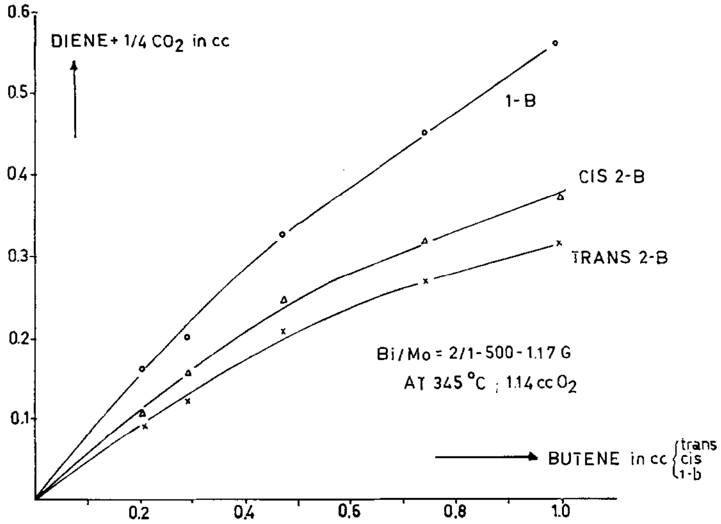

FIG. 13. Comparison of the oxidation activities of *trans*-2-butene, *cis*-2-butene, and 1-butene on the Bi/Mo = 2/1 catalyst at 345°C.

For calculation of the activation energy, we neglected, in first instance, this deviation (the origin of which is discussed below) and we handled our data from the Figs. 8, 9, and 10 in the usual way, i.e., a zero-order kinetic in oxygen and a first-order kinetic in 1-butene. The results are summarized in Fig. 12 in which the activation energy of 10 kcal $mole^{-1}$ was found, hence almost equal to those found earlier. The deviation in the first-order dependency of butene might be attributed to inhibition of the oxidation by the products: isomers, steam, or butadiene. Because of the comparable reactivity of the isomers (see Fig. 13) and the relatively small amounts in which they are produced we do not expect inhibition effects from their presence. The influence of steam on the oxidation of 1-butene was measured at 3 different temperatures and the results are represented in Fig. 14, which shows that a considerable amount of steam does not affect the oxidation: the small decrease in the formation of oxidation products might be a consequence of the small increase in the isomerization products, but more probably might be attributed to a decrease of contact time. The only possibility remaining is inhibition by butadiene. Figure 15 represents the results of inhibition experiments for the 3 types of catalysts, and it shows that the diene inhibition is present for all

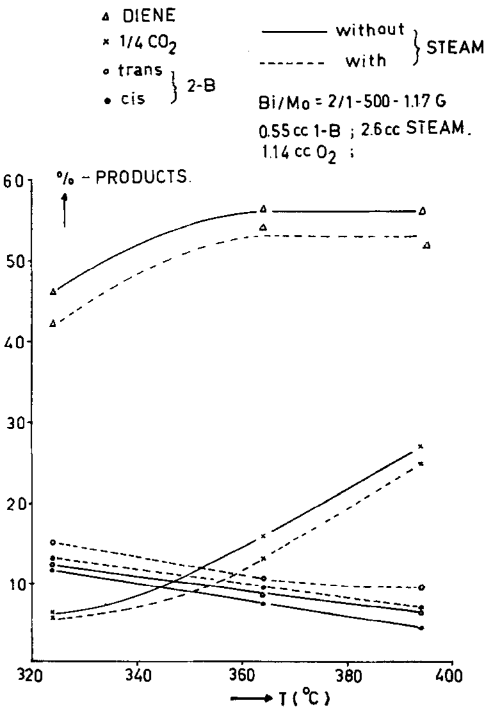

FIG. 14. The influence of steam on the formation of oxidation products on the Bi/Mo = 2/1 catalyst at different temperatures.

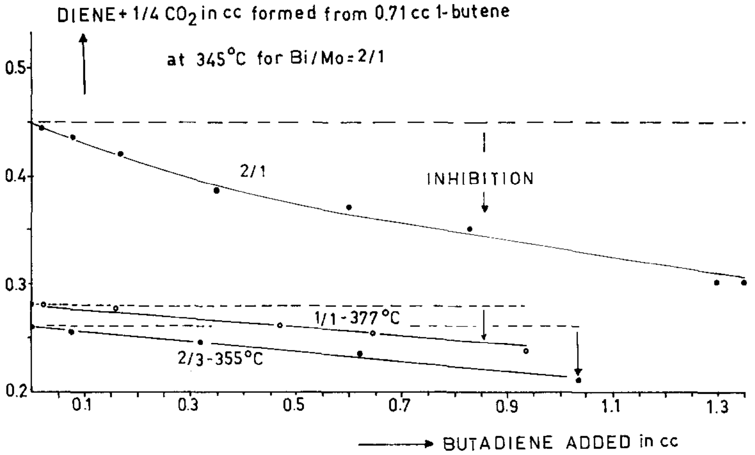

FIG. 15. The decrease in the formation of oxidation products as function of the amount of butadiene added.

three, but is more pronounced for the $Bi_2O_3 \cdot MoO_3$ catalyst. For instance, when 0.7 ml of butene, with a normal production of 0.45 ml of diene + $\frac{1}{4}CO_2$ at 345°C, is contaminated with 0.7 ml of diene, the formation of oxidation products is reduced to almost half this value. Because of these results, we were interested in the value of the activation energy in the presence of higher amounts of butadiene. Pulses of butene and oxygen, mixed with diene, were injected to the catalyst at different temperatures and we calculated the conversion of butene under these conditions with use of Method 1. From these results, again with a zero-order kinetic in oxygen and first-order kinetic in butene we calculated the activation energy as function of reaction temperatures (see Fig. 16). As shown, a curved line is obtained with a high activation energy in the low temperature range and a tendency to smaller values at higher temperatures. It is therefore believed that at higher temperatures the inhibition effects disappear.

ACTIVITIES AND SELECTIVITIES OF THE 3 TYPES OF CATALYSTS

The differences in the activities of these catalysts are shown in the Arrhenius plots in Fig. 12, which shows that the Bi/Mo = 2/1 catalyst is more active than the others. The activities of the others are almost equal. To decide about the selectivity of the oxidation reaction, we have to distinguish two types: (i) the selectivity with respect to isomerization, and (ii) with respect to complete combustion. As shown in Fig. 17, the isomerization to *trans*- and *cis*-2-butenes is obviously the highest with the

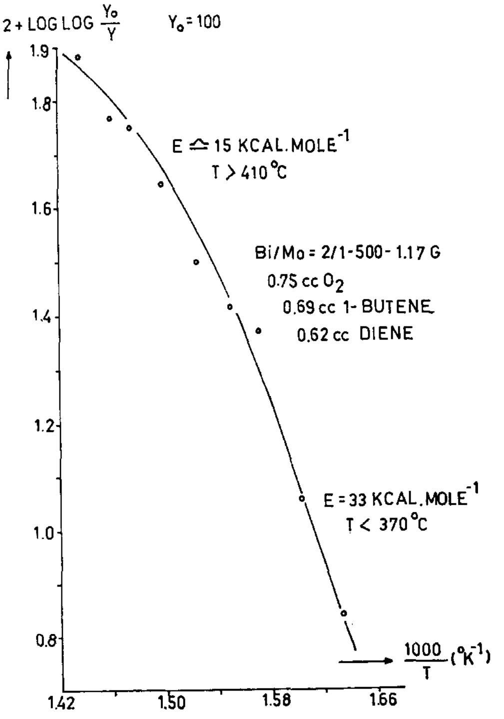

FIG. 16. The Arrhenius plot of the Bi/Mo = 2/1 catalyst when butadiene is admixed to pulses of butene and oxygen.

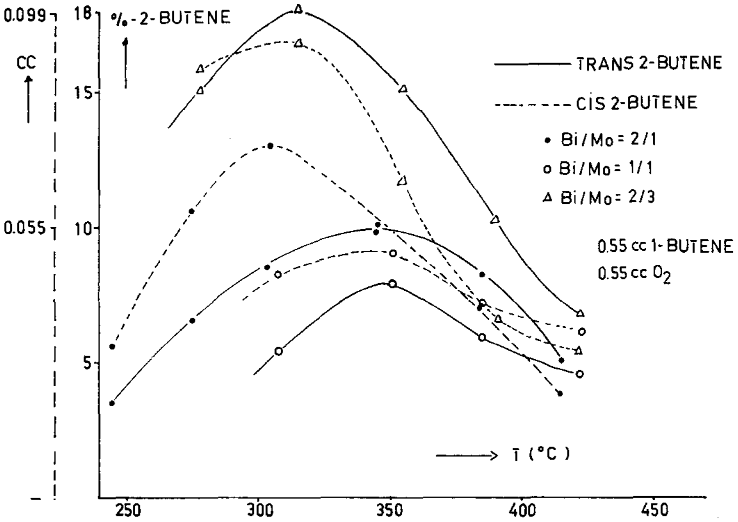

FIG. 17. The isomerization as function of temperature for the 3 types of catalysts.

Bi/Mo = 2/3 catalyst. The *cis/trans* ratio on this catalyst is shown to be one around 290°C. At higher temperatures the formation of *trans*-butene exceeds that of *cis*-butene.

Much smaller isomerizations are observed on the Bi/Mo = 1/1 catalyst and here the formation of *cis*-2-butene is always higher than that of *trans*-2-butene. On the Bi/Mo = 2/1 catalyst the *cis/trans* ratio is reversed at about 350°C. The combustion is dependent on the reaction temperature and on the amount of oxygen present in the pulse when a constant amount of 1-butene is used. As shown in Fig. 18, with an excess of oxygen on the Bi/Mo = 1/1 catalyst and on the Bi/Mo = 2/1 catalyst, the combustions are continuously increasing with temperature. As also shown in Fig. 18, the Bi/Mo = 2/3 catalyst is different in its behavior with respect to complete combustion.

DISCUSSION

The combined evidence of the "one loop" and "two loops" type of pulse experiments

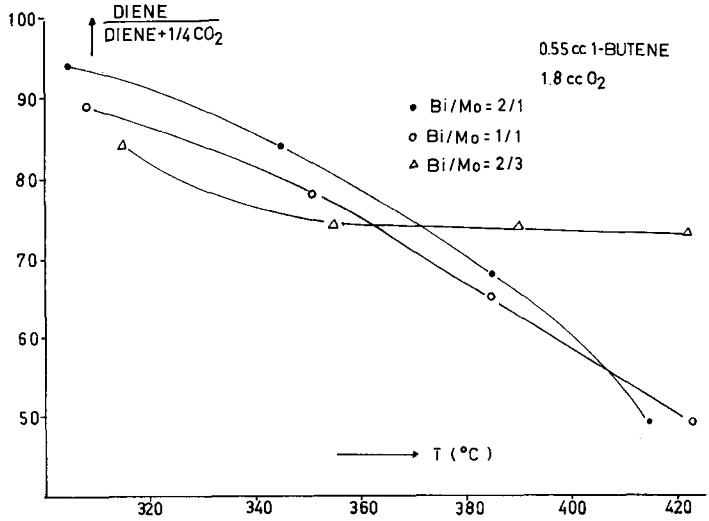

FIG. 18. The selectivity with respect to complete combustion as function of temperature.

prove conclusively that the dehydrogenative oxidation of 1-butene over all types of bismuth molybdate catalysts, measures under pulse conditions, follows the kinetics:

$$\frac{dp_{\text{butadiene}}}{dt} = k \cdot p_{\text{butene}}, \text{ with } k = k_0 \cdot e^{-E/RT}$$

with $E = 10\text{–}11$ kcal mole^{-1}. The rate of the reaction in the absence of oxygen was indeed found equal to that in the presence of oxygen. The reaction is accompanied by two relatively minor reactions: (a) complete combustion that increases in rate with the oxygen pressures, but which can also be discerned in the absence of oxygen; (b) the isomerization to *trans*- and *cis*-2-butene which reaches an optimum at about 300°C and which decreases at higher temperatures. It ultimately must lead to a decreasing rate of oxidation since the 2-butenes are less reactive than 1-butene. However, since we found smaller differences in the rates of *cis*-, *trans*-2-butene, and 1-butene oxidations than earlier reported by Adams *et al.* (*4*), we conclude that the decrease in rate of oxidation is not so important. A far more important point in this connection is the inhibitional effect of the presence of butadiene. For once it is shown to lead to a process with a higher activation energy (33 kcal mole^{-1}), thus possibly explaining the characteristic decrease in activation energy with increasing temperatures noticed earlier (*1*). The inhibition by butadiene at lower temperatures seems to be connected by pronounced complete combustion at the higher temperatures, particularly with the Bi/Mo = 2/1 catalyst.

The proof of the inhibition by butadiene raises the question why its effect was hardly noticed in the experiments without addition of butadiene. Clearly two causes for this discrepancy may be present: (a) the ratio gas/catalyst surface in pulse experiments is relatively low (1 ml of gas/3–4 m^2 g^{-1}) so that adsorption saturation even if possible in principle, is not achieved; and (b) pulse experiments may represent nonstationary situations in which adsorption–desorption processes cannot attain equilibrium conditions. In principle, such a situation may be present for butadiene adsorption–desorption. These considerations indicate the need for additional experiments in which different ratios of gas/solid are present, i.e., either lower or higher; moreover, experiments under stationary conditions appear necessary. We will report on experiments of this type later.

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