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Oxidation of Butylenes and Propylene over Bismuth Molybdate

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The catalytic oxidations of butylenes to butadiene and of propylene to acrolein over bismuth molybdate proceed quite selectively in the range 450–550°C. The reactions are first order in olefin and independent of oxygen and products. The *cis*- and *trans*-2-butene isomers are less reactive than 1-butene. Isomerization by double-bond shift is not rapid. Hydrogen is not oxidized in the system, indicating the reactions are truly oxidative.

INTRODUCTION

The oxidation of normal butene to butadiene over bismuth molybdate has been described by Hearne and Furman (*1*), while the oxidation of propylene to acrolein over a bismuth phosphomolybdate/silica catalyst has been described by Veatch *et al.* (*2*). The cleanness of these reactions and the markedly different products from the two olefins has prompted an examination of kinetics as well as a study of the behavior of related materials which might be involved in the reaction sequence.

A previous paper (*3*) has described oxidation of 1-propene-3-*d*, and has shown that in propylene, the oxidation reaction proceeds by removal of an allyl hydrogen. A similar first step is postulated for oxidative dehydrogenation of *n*-butenes. The use of bismuth molybdate as an oxidation catalyst is not new. It was used over thirty years ago (*4*) for the oxidation of acetylene. However, its use for the selective oxidation of olefins has only recently become prominent.

EXPERIMENTAL

The catalysts used in these studies were precipitated from an ammonium molybdate solution by mixing with acidified bismuth nitrate and ammonia to give a final pH of 5.5 and a bismuth-to-molybdenum atomic ratio of about 1.0. The catalysts were washed with water, dried, then calcined at about 450°C prior to use. The surface area of these catalysts is low, a few square meters per gram, but the activity is very stable for many hours of use.

The testing system used here included a fixed bed in a Pyrex glass or Vycor reactor of 9-mm ID, with a concentric thermowell. The tube could hold a 4-cc catalyst charge and the length of the bed was about 3 inches. Catalyst particle size was normally 10–20 mesh. Frequently, a smaller charge of catalyst was diluted with glass chips of the same size to obtain the 4-cc total volume. The nature of the reactor wall is quite important at temperatures above about 400°C. An 18/8 stainless steel reactor tube caused considerable conversion, mostly to CO_2, when used without catalyst at 480–500°C. Selectivity to acrolein over a bismuth molybdate catalyst at 380°C was lower by about 10% with a stainless reactor than with a glass reactor. More pronounced effects were observed at higher temperatures. Mild steel also gave appreciable reaction at 400°C or above. Pyrex or Vycor tubes gave negligible thermal reaction even up to 690°C.

All of the data were obtained using a flow system at atmospheric pressure. The oxygen source was a mixture of 20 vol % oxygen and 80% argon. The exit gases from the reactor flowed past a heated capillary leak through which continuous sampling of the products could be made to a mass spectrometer. Gas chromatography was used for isomer analyses.

In this paper conversion means percentage of hydrocarbon material fed which is converted to another material (not an isomer), selectivity to a given product means percentage of hydrocarbon material converted which goes to that product, and gas hourly space velocity (GHSV) means total gas volume (STP) fed per bulk catalyst volume per hour. Feed ratios of hydrocarbon to oxygen are molar ratios.

DISCUSSION

The reactions involved are given in the following equations:

$$C_4H_8 + 1/2O_2 \rightarrow C_4H_6 + H_2O \qquad (1)$$

$$C_3H_6 + O_2 \rightarrow C_3H_4O + H_2O \qquad (2)$$

At 700°K reaction (1) is exothermic by about 31 kcal/mole while reaction (2) is exothermic by about 70 kcal/mole. The equilibrium constant is about 10^{13} $(\text{atm})^{0.5}$ at 700°K for (1) and about 10^{21} for (2). These reactions are therefore not hindered by equilibrium limitations.

Some typical kinetic runs with 1-butene are shown in Fig. 1, where the appropriate functions of butylene conversion and space velocity are plotted for a first order rate equation. The data obtained are shown as circles and these results do not obey first order kinetics. However, there is some isomerization of the unreacted butene to 2-butene. At 81% conversion (3600 GHSV) only 48% of the unreacted olefin was 1-butene with equal amounts of *cis*- and *trans*-2-butene formed. It will be shown below that 2-butene reacts much more slowly than 1-butene so that the apparent slowdown in rate indicated in Fig. 1

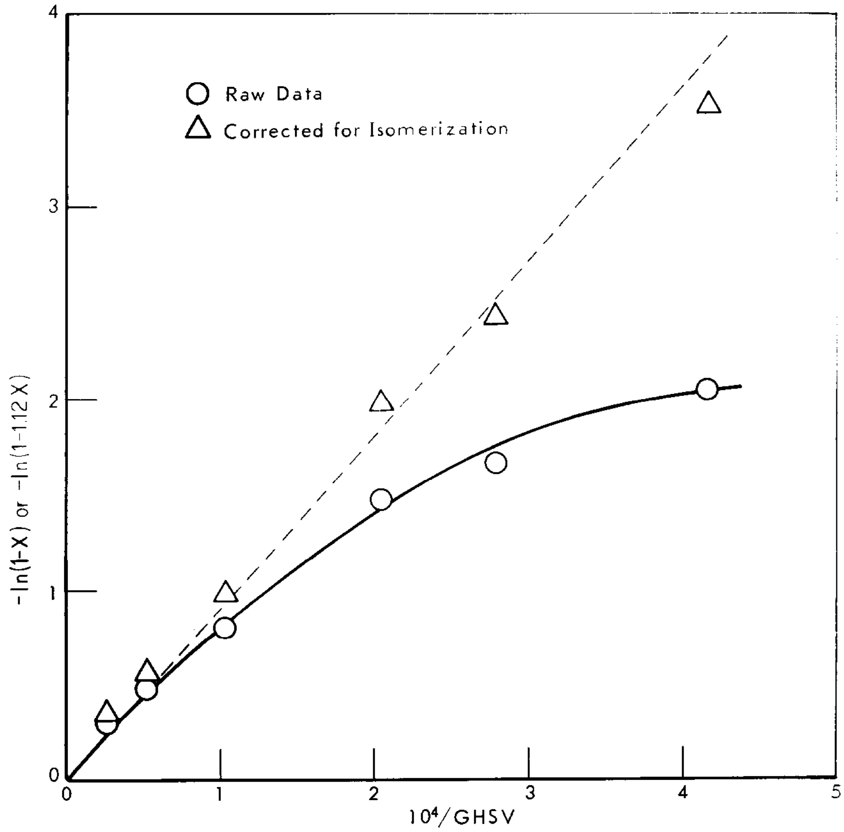


FIG. 1. Kinetics of 1-butene oxidation over bismuth molybdate at 460°C ($C_4H_8/O_2 = 1$).

can be due to isomerization to the less reactive 2-butene. If one neglects the rate of reaction of 2-butene relative to 1-butene and assumes first order reactions for oxidation and isomerization, the ratio of the rate constant for 1-butene isomerization (k_i) to 1-butene oxidation (k_o) is merely the ratio of the 2-butene formed to the total oxidation products formed. This value is 0.12 for the analysis given. The rate of disappearance of 1-butene will be first order with a rate constant of ($k_i + k_o$). The appropriate function to plot can be shown to be $\ln(1 - 1.12X)$ instead of $\ln(1 - X)$, where X is the fractional oxidation conversion. This corrected function is shown plotted in Fig. 1 as triangles. The straight line obtained indicates that the reaction is first order in olefin.

When the amount of oxygen in the feed is varied by a factor of five by varying ratios of $C_4H_8/(O_2 + Ar)$, the rate of 1-butene reaction is unaffected, so long as there is enough oxygen for the reaction. Decreasing the total space velocity by a factor of six from that at which the oxygen was just used up affected neither the butene conversion nor the butadiene selectivity, indicating that the oxygen is essential for reaction and that the hydrocarbons are neither degraded nor dehydrogenated in the absence of oxygen. There also was no effect on activity or selectivity when 20% steam was added to the feed. There was no effect when molecular hydrogen was added to the feed, nor was the hydrogen oxidized, either in the presence of the olefin or when fed alone with oxygen. This means that the reaction is a true oxidation, not a dehydrogenation followed by oxidation of the hydrogen. The apparent activation energy for the oxidation of 1-butene was 26 kcal/mole

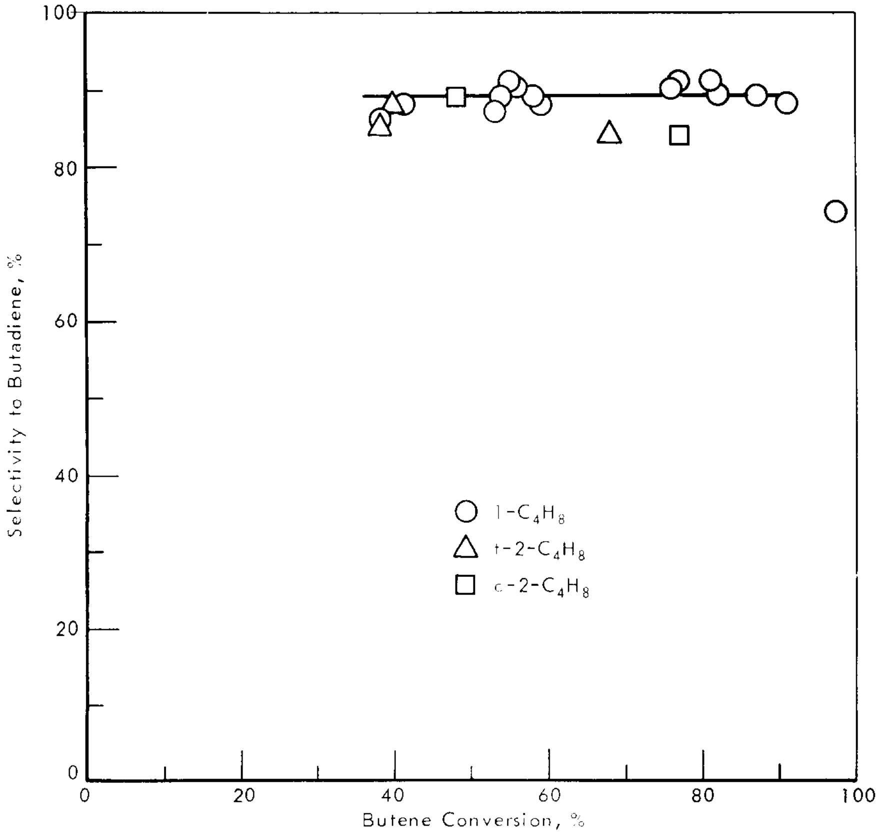


FIG. 2. Oxidation of butene isomers over bismuth molybdate at 460°C.

TABLE 1

OXIDATION OF NORMAL BUTENES OVER BISMUTH MOLYBDATE[a]

Run No.	223				231			288	
Cut No.	1	2	3	4	1	2	3	1	2
Butene isomer fed	1-	*t*-2	*t*-2	*t*-2	*c*-2	*c*-2	*c*-2	1-	*t*-2
Temp (°C)	467	461	462	493	461	464	494	460	460
GHSV/100	36	36	18	18	36	18	18	36	36
Conversion (%)									
O_2	53	28	40	54	37	50	63	64	36
C_4H_8	82	40	68	79	48	77	86	81	38
Selectivity (%)									
Butadiene	89	88	84	83	89	84	82	91[b]	85[b]
Furan	2	0	3	4	2	4	4	2	2
CO_2	3	3	5	5	3	5	5	3	3
CO	2	4	5	4	3	3	4	1	3
Other	4	5	3	4	3	4	5	3	7
Analysis of unconverted C_4H_8 (%)									
1-	52	5	10	7	10	12	7	48	6
trans-2-	24	86	70	79	14	32	36	26	84
cis-2-	24	9	20	14	76	56	57	26	10

[a] Atmospheric pressure; 10–20-mesh catalyst, diluted to 4 cc with glass chips. Oxygen fed as 80% argon, 20% O_2. $C_4H_8/O_2 = 1$. Catalyst bulk density 1.5 g/cc. Catalyst volume 2 cc.

[b] Butadiene contained about 1.5% 1,2-C_4H_6.

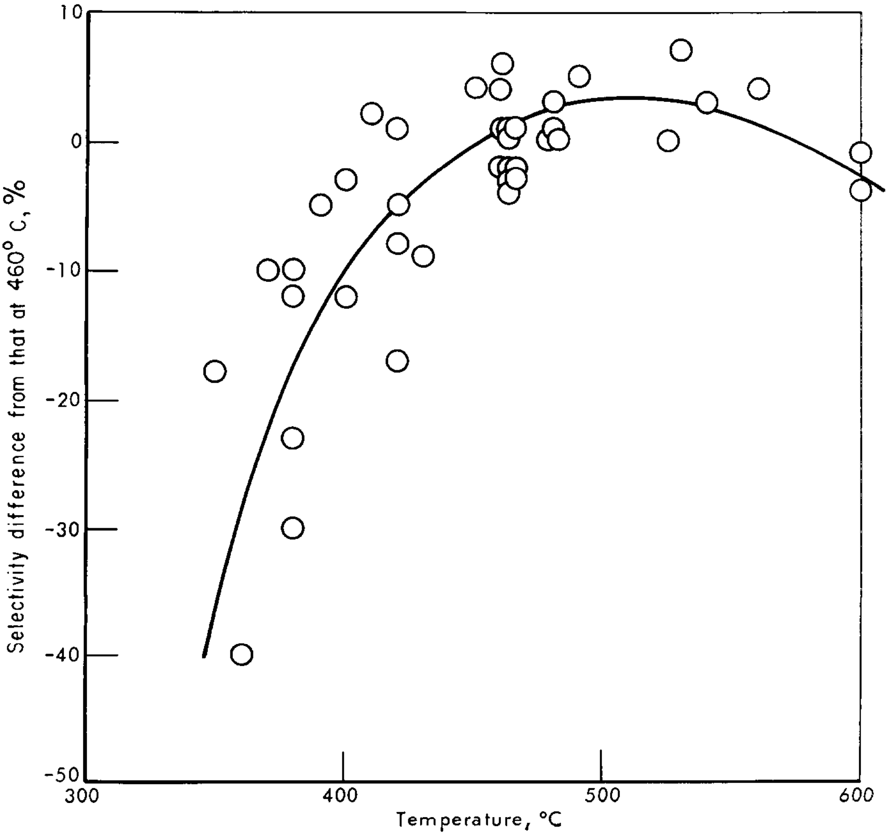


FIG. 3. Effect of temperature on selectivity to butadiene.

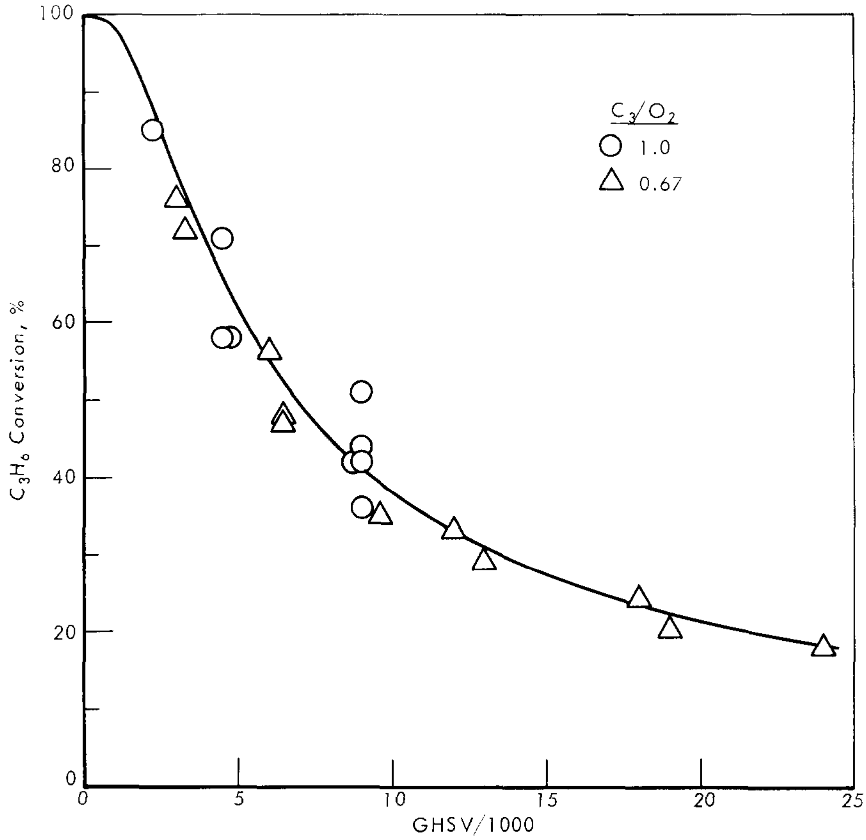


Fig. 4. Effect of total space velocity on propylene conversion by bismuth molybdate at 460°C. Curve calculated for reaction first order in C_3H_6; points experimental.

in the range 345–500°C. Above this temperature the catalyst begins to lose activity, apparently because of structural collapse. The activity is completely destroyed by heating to 700°C.

The isomers of 2-butene are substantially less reactive than 1-butene. At 460°C and 3600 GHSV, *trans*-2-butene gave 38% conversion, with 84% of the unreacted butene as *trans*-2-butene, 10% as *cis*-2-butene, and 6% as 1-butene. Comparing this value with those given in Fig. 1 for 1-butene indicates that the reactivity of *trans*-2-butene is 0.19 relative to 1-butene. This value is an upper limit due to possible isomerization to the more reactive 1-butene. Under these same conditions, the conversion of *cis*-2-butene was 48%, with 76% of the unreacted butene as *cis*-2-butene, 14% as *trans*-2-butene, and 10% as 1-butene. The reactivity of *cis*-2-butene is therefore about 0.26 relative to 1-butene.

Selectivity data at 460°C are given in Fig. 2 and Table 1. The reaction is quite selective, even at high conversions. The line drawn in Fig. 2 is at 89% selectivity. The selectivity drops at conversions above 90%. The 2-butene isomers form butadiene at somewhat less selectivity at conversions of 70–90% than does 1-butene, due to the lower reactivity of these olefins. The by-products are mainly carbon oxides, with small amounts of methyl vinyl ketone, furan, acetone, propylene, ethylene, and formaldehyde. One of the reasons for the high selectivity of this system is the stability of the butadiene formed. Butadiene was fed with air over the catalyst at GHSV = 1800 at 490°C. Butadiene conversion was 36% with 25% selectivity to furan and

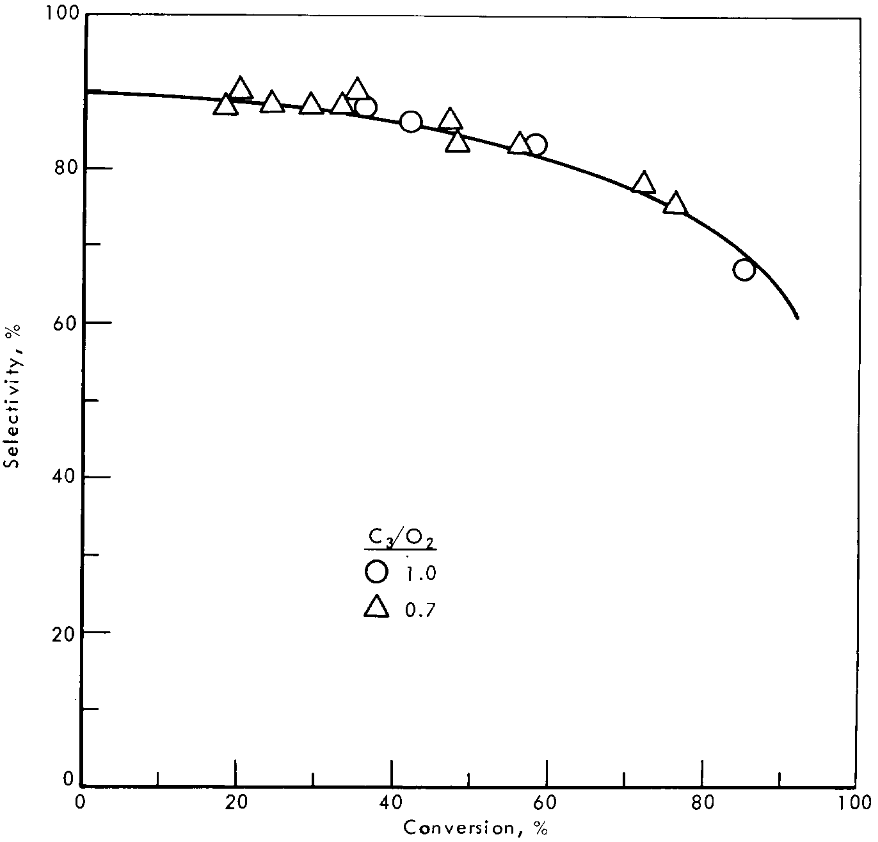


FIG. 5. Effect of propylene conversion on acrolein selectivity for bismuth molybdate, 460°C.

60% selectivity to carbon oxides. The rate of oxidation of butadiene is of the order of 1/20th of the rate of oxidation of 1-butene. Direct oxidation of *n*-butenes to CO_2 is also about 1/20th as fast as the oxidation to butadiene.

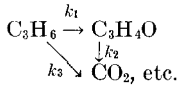
The effect of temperature on the selectivity of oxidation of 1-butene is shown in Fig. 3, where the difference in selectivity from that obtained at 460°C (at the same conversion) is given as a function of temperature. The optimum temperature for best selectivity is 450–550°C.

Butane and isobutane are essentially inert in this system. At 600°C and GHSV = 900, butane was converted only 34%, the products being mainly carbon oxides. Isobutane at 550°C and GHSV = 450 gave 15% conversion, again mainly to carbon oxides.

Isobutylene gives methacrolein quite selectively. At 450°C and GHSV = 3600, isobutylene conversion was 55% and selectivity to methacrolein was 80%.

The oxidation of propylene over bismuth molybdate is first order in propylene and independent of oxygen and products, as illustrated in Fig. 4, where the curve is that calculated for the stated kinetics. The rate constant was chosen to give best visual fit. Greater variations in oxygen concentration from that given in Fig. 4 did not alter the rate nor did addition of 20% steam to the feed. Molecular hydrogen had no effect on the reaction, nor was the hydrogen oxidized. The apparent activation energy over the range 350–500°C was 20 kcal/mole. Structural changes affect the activity of the catalyst above about 500°C. The rate of reaction of propylene relative to 1-butene, as measured over the same catalyst, was 0.11.

A conversion–selectivity plot is shown in Fig. 5. Selectivity declines at higher conversions, but it does not extrapolate to 100% at zero conversion. This can be explained by a combination of parallel and consecutive reactions given in Eq. (3).



$$\begin{tikzcd} C_3H_6 \arrow[r, "k_1"] \arrow[dr, "k_3"'] & C_3H_4O \arrow[d, "k_2"] \\ & CO_2, \text{ etc.} \end{tikzcd} \qquad (3)$$

The line drawn in Fig. 5 is calculated assuming all the reactions are first order and for $k_3/k_1 = 0.10$ and $k_2/k_1 = 0.25$. The main by-products were carbon oxides, acetaldehyde, and formaldehyde.

The effect of temperature on the selectivity to acrolein is shown in Fig. 6. Best selectivity is obtained in the range 460–520°C. This is about the same region as found optimum for butylene oxidation.

CONCLUSIONS

The oxidations of the butylenes and propylene over bismuth molybdate occur quite selectively and the kinetics are simple. The similarity in kinetics, activation energies, and selectivity–temperature effects indicate that the same mechanism is involved in the formation of diene or of unsaturated aldehyde. Both reactions are clearly oxidative and do not involve simple dehydrogenation. The variation of reactivity with different olefins indicates that the structure of the olefin is quite important in the formation of the activated complex. Indeed, kinetic studies with other olefins (*5*) have indicated that the slow step involves the

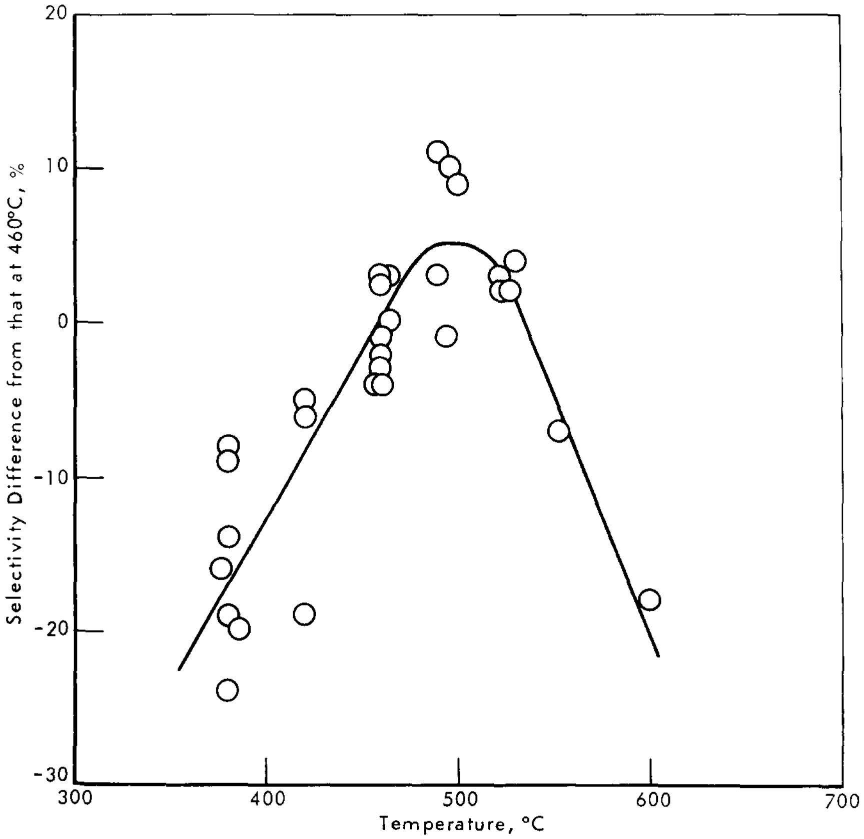


FIG. 6. Effect of temperature on selectivity to acrolein.

abstraction of an allylic hydrogen atom by an adsorbed oxygen atom, the speed of this step being inversely related to the allylic carbon–hydrogen bond energy.

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