

## Oxidation of 1-Butene Over $\text{UO}_3\text{-Sb}_2\text{O}_3$ Catalysts

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The oxidative dehydrogenation of butene to butadiene over U-Sb catalysts was investigated. The presence of two compounds, reported by Grasselli and Callahan, was confirmed with one being the actual catalyst. The reaction is first order in butene and zero order in oxygen. In the absence of oxygen, interaction of butene with the catalyst oxygen occurred but only to a minor degree, the interaction being confined to the surface. Partial reactivation by heating of a catalyst inactivated by the interaction with butene in the absence of  $\text{O}_2$  could be effected, but there exists a tendency for the catalyst to decompose. A remarkable detail in the kinetics is that, contrary to the reaction over Bi-Mo catalyst, double-bond isomerization is absent.

### INTRODUCTION

Grasselli and Callahan (1) recently published a paper on the properties of U-Sb oxide catalysts with respect to the formation of acrylonitrile from propene and  $\text{NH}_3$ . The actual SOHIO catalyst (2) is supported by silica, but numerous runs were reported in the paper on nonsupported samples in fixed-bed microreactors. One of the most important items in their report concerns the identification of two different U-Sb compounds,  $(\text{UO}_2)\text{Sb}_3\text{O}_7$  and  $\text{Sb}_3\text{U}_3\text{O}_{14}$ , of which only the former proved active and selective for the oxidation. X-Ray diagrams of the two compounds were given, but the actual information concerning their structures was obtained from a thorough investigation of the infrared (ir) spectra. It is from these spectra that the first phase is considered to be a uranyl antimonate and the second an antimony-uranate.

We have also investigated the U-Sb catalyst with the purpose of comparing its activity pattern and kinetics for the oxidative dehydrogenation of butene to butadiene with that of the earlier investigated Bi-Mo catalyst. Since it differs considerably in these respects we believe

it informative to present our data here as complementary to those of Grasselli and Callahan. We also observed the two compounds, but the data of our American colleagues are far more informative and we shall not, therefore, consider our results in this connection in any great length except to show our agreement with their data.

### EXPERIMENTAL

#### *Preparation of Catalysts*

**Method 1.** A certain amount of  $\text{Sb}_2\text{O}_3$  was weighed and dissolved in a solution of HCl under slight heating after which a solution of uranyl acetate of known concentration was added to it, resulting in the formation of a green solution. Adding a solution of  $\text{NH}_4\text{OH}$  to pH 7-8 produced an orange to yellow-brown precipitate depending on the ratio Sb/U. The slurry was heated for 8 hr at 90-100°C, and subsequently decanted. The precipitate was repeatedly boiled with water, filtered, and washed on the filter until free of  $\text{NH}_4\text{Cl}$ , dried for 12 hr at 110°C, and sintered for 16 hr at 725°C. Proceeding in this way, samples of Sb/U ratios of 0.5, 1.0, and 2.0

up to 10.0 were prepared. The colors of the solids varied from dark green (excess of U) via blue-violet (Sb = 1-2) to yellow-brown (excess of Sb).

**Method 2.** Liquid  $\text{SbCl}_5$  was added to concentrated HCl in known amounts. To this solution was added a solution of uranyl acetate after which it was processed similarly as described above. Difficulties were encountered in the filtering stage since the precipitates were gel-like. The product after drying proved very hard. The colors of the samples were similar to those reported above.

**Method 3.**  $\text{Sb}_2\text{O}_5$  was dissolved in molten KOH after which the melt was poured into water. To this solution was added a solution of uranyl acetate after which neutralization followed with HCl. The precipitate was filtered, washed, dried, and subsequently sintered at  $700^\circ\text{C}$ . An amount equal to 20 g was prepared for every sample.

Some remarks in connection with the method of preparation should be added here. First, a thorough removal  $\text{NH}_4\text{Cl}$  in the wet state is definitely necessary since removal by heating leads to a simultaneous loss by sublimation of antimony oxide and/or uranium oxide. The samples prepared according to Method 3 proved catalytically inactive and were not investigated further. All the others were studied by X-ray diffraction using  $\text{CuK}_\alpha$  radiation and a Ni filter. Surface areas were measured with an areameter.

#### *Testing of Catalyst Activity and Selectivity*

Activity and selectivity of the various samples were tested according to three methods, similar to those described by Keizer and Batist (3) (pulse method) and Prette and Batist (4) (continuous flow and recirculation). In view of the similarity of our apparatus and testing methods to those applied by these authors we shall restrict the description to some quantitative details.

**Continuous flow.** One g of catalyst was used; bed height about 2 cm. "Artificial air," 80% He and 20%  $\text{O}_2$  was the source

of oxygen. Butene was added in the ratio  $\text{C}_4/\text{O}_2 = 1/55$  vol/vol.

**Total gas rate, 70  $\text{cm}^3/\text{min}$ .** Pressure in the reactor was approximately 1 atm. Runs were made with increasing and subsequently decreasing temperature to ascertain whether the catalyst activity remained constant during the test period.

**Recirculation.** Only the catalyst Sb/U = 4, prepared according to Method 1 was investigated in this way. Catalyst amount: 0.5 g (20-40 mesh), total volume of reaction system  $217 \text{ cm}^3$ , recirculation speed  $200 \text{ cm}^3/\text{min}$ . Amounts of gases introduced in a normal run:  $29 \text{ cm}^3 \text{ O}_2$  and  $29 \text{ cm}^3$  1-butene. After every run, the system was purged with helium and subsequently filled with  $\text{O}_2$  after which the catalyst was regenerated for 1 hr at  $600^\circ\text{C}$ .

**Pulse.** Only catalyst Sb/U = 4, Method 1 was investigated by this method. Amount 0.5 g (20-40 mesh). Carrier gas: He,  $56 \text{ cm}^3/\text{min}$ . Pressure in reactor, 2.5 atm, pulse volume, 0.5 or  $1.0 \text{ cm}^3$ . Before introducing butene, the catalyst was pretreated with a number of oxygen pulses until no  $\text{O}_2$  was no longer taken up or  $\text{CO}_2$  formed.

#### *Analysis of Reaction Products*

The reaction products were determined by room-temperature gas chromatography, column length, 8 m; diameter, 4 mm interior, 6 mm exterior. Carrier gas, helium, carrier material, Chromosorb (30-50 mesh), stationary phase 2,4-dimethylsulfolane (20 wt %). Detection: thermal conductivity, current, 200 mA, peak area determined by an integrator. Rate of carrier gas stream  $40 \text{ cm}^3/\text{min}$ , column pressure 1-1.5 atm. Average time for an analysis, 15 min, necessitating the use of sample valves. Relative sensitivity for the various gases:  $\text{O}_2$ :1.00,  $\text{CO}_2$ :1.29, 1-butene:2.16, 2-butene:2.16, butadiene:2.11.

It should be mentioned here that the Sb-U catalyst *does not give rise to any double-bond isomerization*, in strong contrast with the Bi-Mo catalyst. This makes the analysis of the reaction much simpler and can be considered a characteristic property of the catalyst.

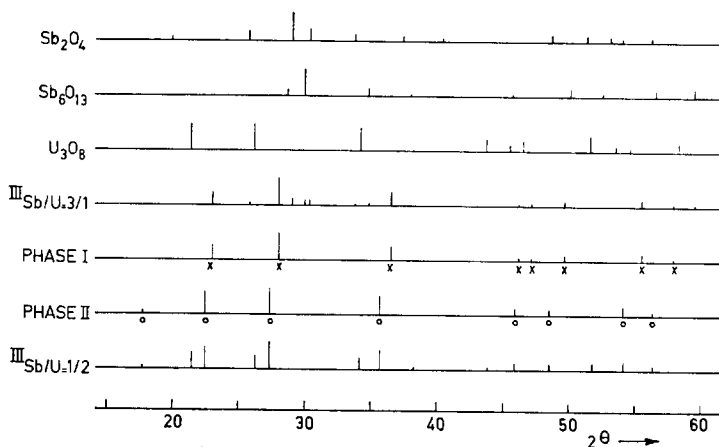


FIG. 1. X-Ray diagrams of various compounds encountered in samples prepared according to Method 1. Phase I and phase II similarly indicated as by Grasselli and Callahan (1).

## RESULTS

### (1) X-Ray Diffraction

The results obtained here were very similar to those reported by Grasselli and Callahan and differed only in the fact that in some of our samples we observed  $Sb_6O_{13}$  which was apparently absent in their preparations. In Fig. 1 we have given the diagrams for the phases determined by us from the samples prepared according to Method 1, indicating the binary compounds by the nomenclature adopted by Grasselli *et al.* Figure 2 shows the diagrams of the samples with Sb/U increasing from 0.5 to 10, and Fig. 3, shows approximate

concentrations of the various phases as derived from the intensity of their strongest lines. Figure 4 shows similar diagrams for the preparations according to Method 2: It is seen that they only consist of  $Sb_6O_{13}$  and compound II of Grasselli *et al.* both compound I and  $Sb_2O_4$  are missing.

### (2) Activity and Selectivity Measurements in Continuous Flow Experiments

The general character of the results appears to be determined in the first instance by the method of preparation and the Sb/U ratio. Figure 5 compares the behavior of two catalysts with an Sb/U ratio of 4 but prepared according to the different methods.

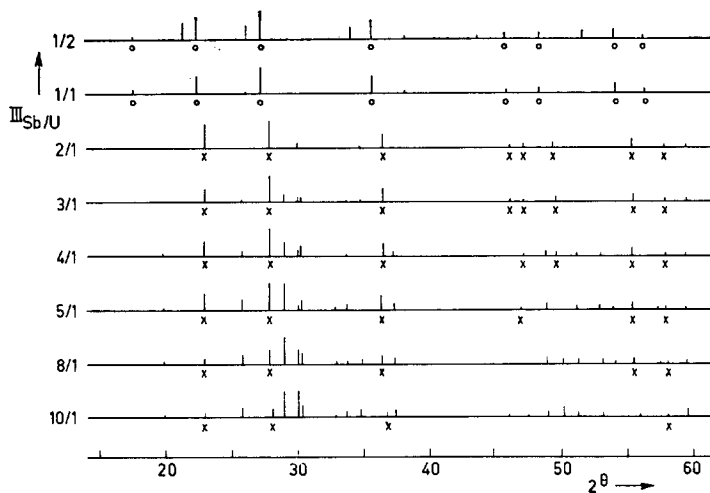


FIG. 2. X-Ray diagrams of samples prepared according to Method 1.

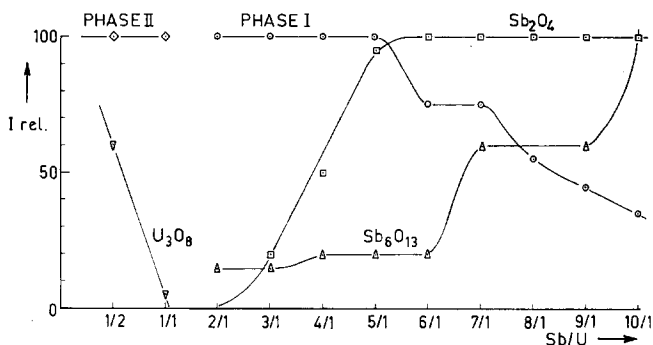


FIG. 3. Approximate concentrations of various compounds prepared according to Method 1.

The sample prepared according to Method 2 shows a low activity at temperatures below 350°C and then suddenly begins to show a fast conversion that produces large amounts of CO<sub>2</sub>. The selectivity of the conversion, defined by

$$S = \frac{\% \text{ butene converted to butadiene}}{\% \text{ butene converted to CO}_2 \text{ and butadiene}}$$

drops to around 0.5 at the temperature at which the catalyst begins to show an activity and remains roughly constant at higher temperatures.

The sample prepared according to Method 1 shows a more gradual increase in conversion while its selectivity remains high, even at higher temperatures. An X-ray investigation of the Type 2 catalyst after the activity run showed that it was decomposed in the course of the experiment (see Fig. 6) into U<sub>3</sub>O<sub>8</sub> and Sb<sub>2</sub>O<sub>4</sub>. Since the samples prepared according to Method 2 show compound II to be present, even at high Sb/U ratios, the possibility arose that the peculiar behavior of the Type 2 sample was caused by the presence of this

compound. Accordingly, the sample with Sb/U = 1 but prepared according to Method 1 was exposed to the same test and indeed showed a completely similar behavior. In this case the decomposition could even be followed visually from the change in color from blue-violet to green. It can, therefore, be concluded that compound II decomposes during the catalytic oxidation.

This decomposition leads to a peculiar behavior that is illustrated in Fig. 7. The catalyst begins to react slowly in a process that is fairly selective, but at a temperature around 360°C, the activity increases steeply while the selectivity drops in a marked manner. Decreasing the temperature does not lead to any change in either the conversion or the selectivity until a temperature of 150°C is reached after which the reaction suddenly stops. This reaction pattern is characteristic for the presence of U<sub>3</sub>O<sub>8</sub> as is also shown in Fig. 7, where the hysteresis loop is clearly demonstrated.

Catalysts prepared according to Method 1 but with a Sb/U ratio lower than 4 are also unstable during operation although

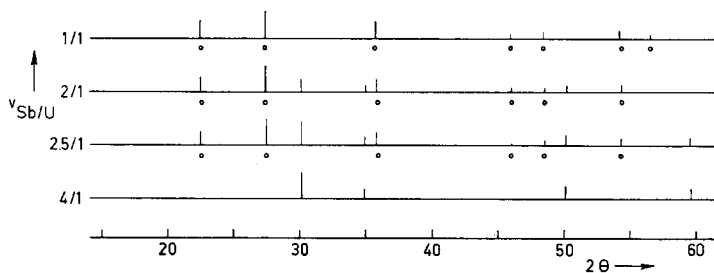


FIG. 4. X-Ray diagrams of samples prepared according to Method 2.

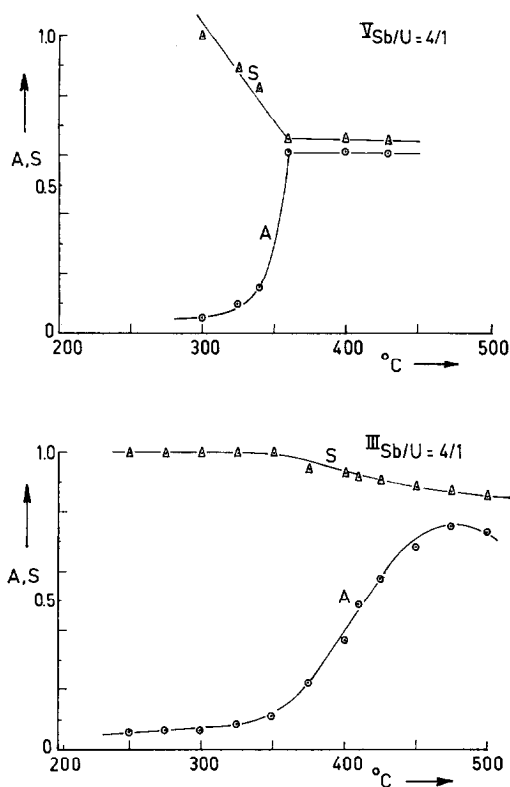


FIG. 5. Comparison of activity and selectivity of two catalysts Sb/U = 4/1 prepared according to Methods 1 and 2.

their rate of decomposition is lower. It is only at ratios equal or higher than 4 that they become sufficiently stable to allow reproducible measurements. From 4 to 10 there can be observed a steady decrease

in activity, but the selectivities remain invariably high (Fig. 8). Further measurements have, therefore, been limited to the Sb/U = 4 sample (Method 1). Since the concentration of compound I is still relatively high at this ratio the conclusion of Grasselli and Callahan that compound I in the active catalyst appears fully substantiated by the new experiments.

The conversion over this catalyst measured as a function of the temperature is shown in Fig. 9. The selectivity (Fig. 9a) is high so long as the temperature remains below 400°C, but above this limit, there is considerable formation of CO<sub>2</sub>. If we assume the reaction to obey a first-order dependency on the partial pressure of butene, an assumption that will be substantiated later on, the conversion as a function of the temperature is found to follow an Arrhenius law (Fig. 9b) with an activation energy of 22 kcal mole<sup>-1</sup>, provided the temperature remains above 350°C. At lower temperatures, there arises a strong bend in the log *k* vs 1/*T* relation compatible with a much lower activation energy.

### (3) Rate Measurements under Recirculation

Figure 10 shows the conversion as a function of time in the recirculation apparatus for mixtures of a butene/O<sub>2</sub> ratio = 1 at various temperatures and for the Sb/U = 4 catalyst. At *T* lower than 350°C,

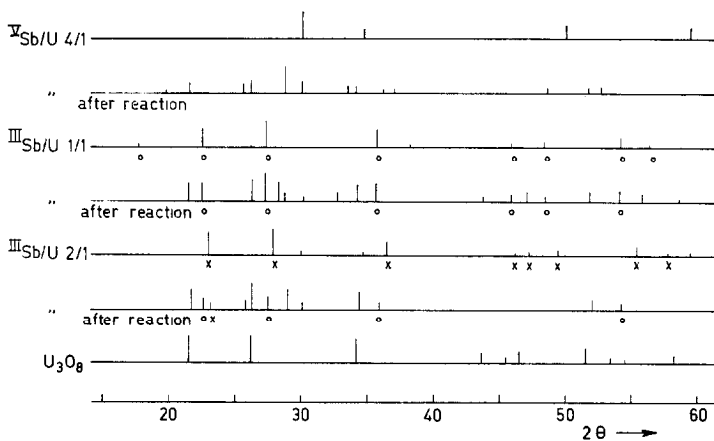


FIG. 6. X-Ray diagram of catalyst samples before and after reaction.

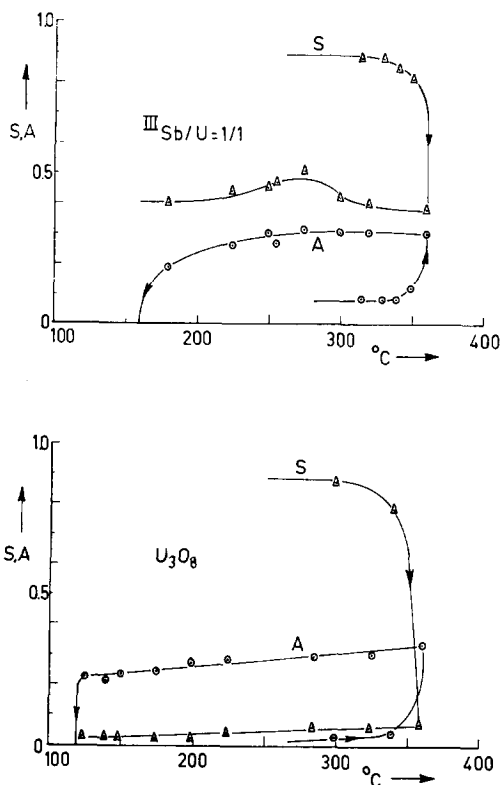


FIG. 7. Conversion and selectivity for some catalyst samples as measured with increasing and decreasing temperature.

there are signs of inhibition by the products, since the conversion stops before all the reactants have been consumed. The inhibiting substance is not butadiene since an

admixture of this compound to the reaction mixture did not alter the rate in an appreciable manner (Fig. 10a). It did, however, increase the rate of formation of  $\text{CO}_2$  in a marked manner indicating that complete combustion starts from this substance. The result in Fig. 10b show that the rate is independent of the partial oxygen pressure but depends on the partial pressure of butene.

It was observed during these experiments that the catalyst activity tended to decrease in the course of time, a decrease that was more marked if butene was present in excess. This phenomenon was particularly evident after the run with  $14.5 \text{ cm}^3 \text{ O}_2$  and  $29 \text{ cm}^3$  butene in the reactor volume. The reaction stopped after all oxygen was exhausted, but subsequent addition of an extra dose did not lead to further reaction, and the reaction slowly started again. Circulation of pure oxygen over a catalyst thus deactivated it, but then at a temperature of  $600^\circ\text{C}$  produced considerable amounts of  $\text{CO}_2$ : The catalyst surface of a deactivated catalyst, therefore, appears to contain a substance that can only react with oxygen at a higher temperature.

Circulation of pure butene over the catalyst in the temperature range  $340\text{--}420^\circ\text{C}$  did not produce any butadiene, although a small decrease in the pressure was observed. A subsequent exposure to a

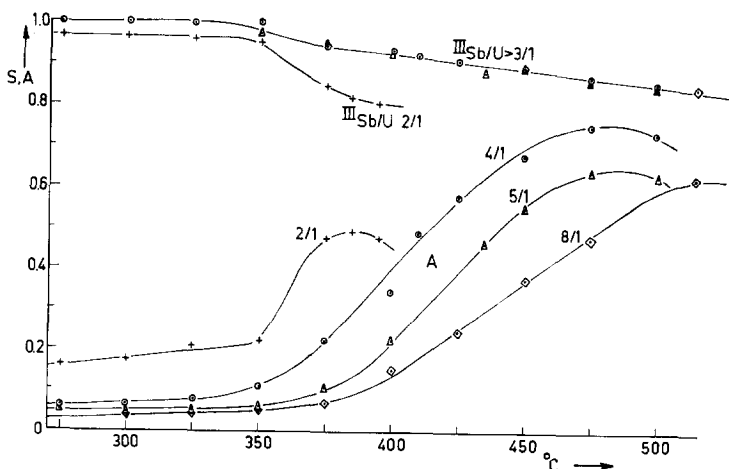


FIG. 8. Conversion and selectivity for samples in the high Sb/U ratios prepared according to Method 2 (continuous flow).

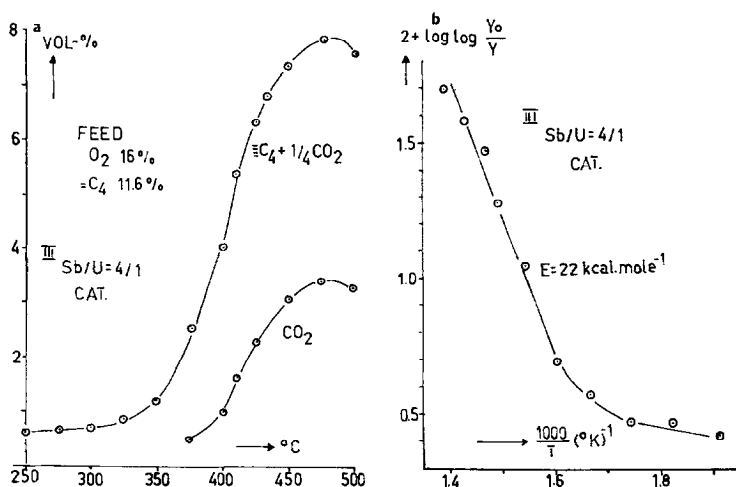


FIG. 9. Continuous flow experiments. (a) Activity and selectivity of Sb/U = 4 catalyst as a function of temperature; (b) Arrhenius plot. C<sub>4</sub> signifies butene, ≡C<sub>4</sub> signifies butadiene.

butene-O<sub>2</sub> mixture showed that it had become inactive consequent to the interaction of the undiluted hydrocarbon. When the inactive catalyst was then heated in He to a higher temperature, a formation of CO<sub>2</sub> was observed, together with signs pointing to a decomposition of the catalyst such as the formation of a white deposit in the cooler parts of the reactor and a change in color from brown to green. After this treatment, the catalytic properties of the catalyst were found to have undergone a drastic change; it was more active but far

less selective than before. Since these characteristics have been shown earlier to be connected with a decomposition of compound I into UO<sub>3</sub> and Sb<sub>2</sub>O<sub>3</sub>, it can be assumed that also in this process decomposition of the catalyst occurred.

#### (4) Results of Measurements under Pulse Conditions (Catalyst Sb/U = 4/1)

The method of investigating the catalytic reaction under pulse conditions consisted in pulsing mixtures of butene and He on the one hand and O<sub>2</sub> and He on the other

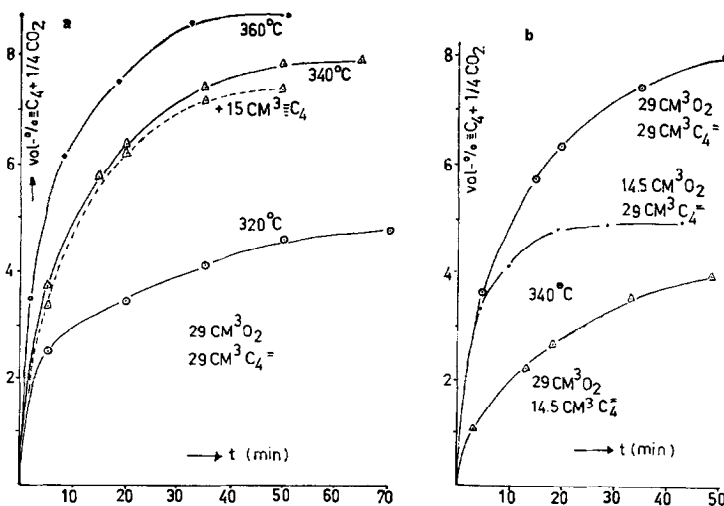


FIG. 10. Recirculation experiments. (a) Conversion as a function of time and temperature. C<sub>4</sub>-/O<sub>2</sub> = 1. (b) Conversion as a function of C<sub>4</sub>-/O<sub>2</sub> ratio at 340°C.

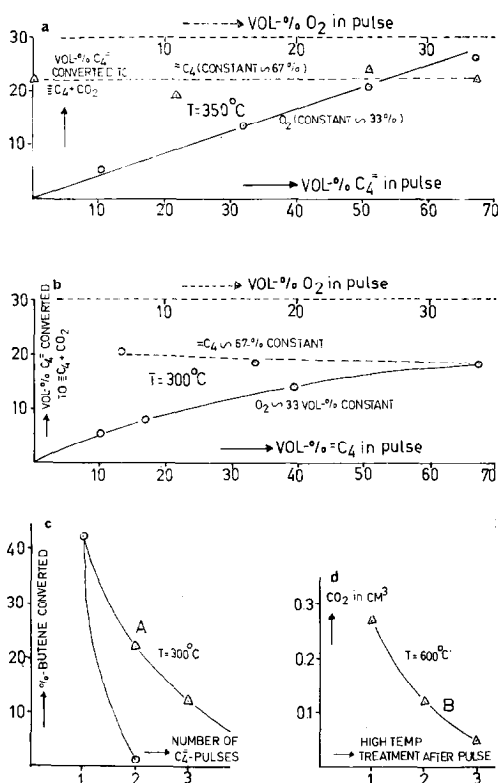


Fig. 11. Pulse experiments. Conversion as a function of partial pressures of C<sub>4</sub> and O<sub>2</sub> at (a) 350°C, (b) 300°C; (c) and (d) are results of experiments in which the catalyst Sb/U = 4 was exposed to butene under the formation of butadiene with complete deactivation and was subsequently reactivated by a treatment in He at 600°C. ○, Conversion before reactivation at 600°C, △, after reactivation. (A) Butadiene formation per pulse; (B) CO<sub>2</sub> formation during high-temperature reactivation.

hand over the catalyst, the mixtures being prepared in advance in sample loops. By manipulating the moments of injection of the two samples they could be made to enter the reactor as a single pulse, the composition of which was defined by that of the separately prepared "hydrocarbon" and "oxygen" sample. Consequently the partial pressures of the various compounds in the pulse could be varied at will.

Figure 11a shows the degree of conversion as a function of the partial pressures of butene and O<sub>2</sub> at 350°C. It shows that the rate of the reaction varies linearly with the butene pressure and is independent

of the oxygen partial pressure. An interesting aspect of these experiments is that they show the conversion to remain the same, even in the complete absence of O<sub>2</sub>. Similar experiments at 300°C show a somewhat less simple picture (Fig. 11b) that can, however, be understood from that at the higher temperatures by assuming the presence of an inhibition by the products at the lower temperatures. The evidence found in the pulse experiments in connection with the interaction of butene and the catalyst in the absence of O<sub>2</sub> seems in conflict with that found in the circulation studies where we found no interaction. Further studies give the solution for this disagreement. If the catalyst is subjected to a second pulse of pure butene after it has been exposed to a first pulse in which the conversion was substantial, no conversion at all was observed in the second pulse. The capacity of the catalyst to react with gaseous butene is, therefore, limited and could be calculated as 0.5 cm<sup>3</sup>/g. Since we knew from the circulation experiments that exposure to butene leaves the catalyst with a certain amount of adsorbed material that could be removed by heating the sample in He at 600°C in the form of CO<sub>2</sub>, a similar treatment was given to the catalyst after the butene pulse. Also here we found the production of CO<sub>2</sub>. After this treatment the catalyst was now found to be partially reactivated: it could now convert about half the amount converted in the first pulse. Repeating this procedure for a number of times (see Fig. 11c,d) showed that after every butene pulse and subsequent high-temperature treatment, the capacity for reaction was halved and so was the amount of CO<sub>2</sub> produced at the higher temperature.

Since the kinetics in pulse experiments were found to be quite simple, although perhaps somewhat difficult to explain, the dependency of the first-order rate constant on the temperature was also determined.

As Fig. 12a shows, a linear log *k* vs 1/*T* relation was found leading to an activation energy of 8 kcal mole<sup>-1</sup>. Actually, as becomes apparent by comparing the conversions given in Fig. 9a for continuous flow



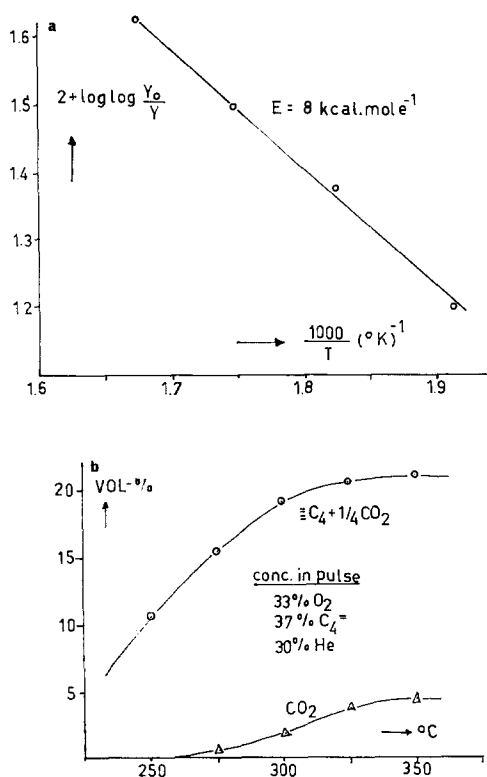


FIG. 12. Pulse experiments. (a)  $\log k$  vs  $1/T$ . (b) Conversion as a function of temperature.

with those in Fig. 12b for pulse conditions the conversion at lower temperatures for the pulse experiments is much greater. Substantial conversion is already present for the pulse experiments in the temperature range below 300°C where the continuous flow experiments showed hardly any conversion, presumably because of the presence of an inhibition by some product.

#### DISCUSSION

A comparison of the oxidative dehydrogenation of butene to butadiene over the Bi-Mo and the U-Sb catalysts shows a number of similarities but also some marked differences. Let us first sum up the similarities.

- (1) In both instances, the catalysts showing the required characteristics of activity together with selectivity are binary compounds. However, not every binary compound of the oxide pairs shows

these characteristics. This demonstrates the necessity to incorporate a combination of properties in the catalyst by the method of combining two different cations but also the necessity to combine them in a suitable configuration.

- (2) In both cases, the rate-determining reaction is that between the hydrocarbon and the oxygen ions of the catalyst. This has been demonstrated by the actual presence of a reaction in the absence of gaseous oxygen and is moreover readily reconciled with the zero-order dependency of the rate on the partial pressure of oxygen.

Differences between the two systems are as follows:

- (1) While the Bi-Mo catalyst can be reduced to a remarkable degree by the hydrocarbon in the absence of oxygen, which phenomenon shows the presence of a fast diffusion in the bulk of the solid, the U-Sb catalyst seems only capable of applying its surface oxygen ions for this purpose. Moreover, while extensive reduction of the Bi-Mo catalyst can be allowed without the catalyst losing its properties to regain its original state after reoxidation, even a slight reduction of the U-Sb catalyst leads to a decomposition of its structure combined with the impossibility to restore its original properties by a reoxidation.
- (2) The U-Sb catalyst, contrary to the Bi-Mo catalyst, does not catalyze the double-bond isomerization of the butenes. Since double-bond isomerization might be connected to the occurrence of an intermediate allyl structure, either the reaction over the U-Sb catalyst does not occur via an allyl intermediate, or, what seems a better assumption, there exist circumstances under which allyl formation does not lead to isomerization.

(3) In both cases an inhibition by products of the reaction is observed. However, the actual characteristics of the inhibitory effects are quite different. On the Bi-Mo catalyst, it is butadiene that forms the inhibitor and as shown by Batist and Prette (4) its action occurs during the reaction of the catalyst by butene. It has been shown that a similar inhibition does not exist for the U-Sb catalyst. The nature of the inhibition in this reaction has not become clear from the experiments reported. There are, however, a few observations that might offer a clue to its nature.

The original reaction mechanism for the oxidation dehydrogenation of butene to butadiene on Bi-molybdates as given by Batist *et al.* (5) can be changed as a consequence of the adsorption measurements of Matsuura and Schuit (6), who found two types of adsorption sites, the simultaneous presence of both being necessary for the reaction.

Site A is an  $O^{2-}$  ion that seems to adopt the two H atoms dissociated and that can dissociate as  $H_2O$  leaving an anion vacancy at the surface. The anion vacancy accepts the  $O_2$  necessary to reoxidize the reduced catalyst. If the  $O^{2-}$  ion is present it can adsorb butadiene that then may react further to  $CO_2$  in a slow reaction, necessitating other  $O^{2-}$  ions different in properties from those in site A. Site B is a combination of two  $O^{2-}$  ions and one vacancy. These  $O^{2-}$  ions possess properties that are different from those on site A. The combination of sites can adsorb olefines, either as a  $\pi$ -bonded complex at the vacancy or by a  $\sigma$ -bonded allyl intermediate with one of the two  $O^{2-}$  ions, the other being occupied by the H atom dissociated. The  $O^{2-}$  ions are not removed from the catalyst structure by the reduction. Measurements by Matsuura to be reported later have given a partial explanation of the differences between the  $UO_3-Sb_2O_3$  and the  $Bi_2O_3-MoO_3$  catalysts. Also here two

types of reaction centers could be observed. The site most similar to  $O_A$  on  $Bi_2O_3-MoO_3$  was found to be difficult to regenerate by  $O_2$  once it was removed, because there was no fast adsorption on  $UO_3-Sb_2O_3$  after incipient reduction, contrary to the  $Bi_2O_3-MoO_3$  case. This could be explained by a strong adsorption of an oxygenated product on the vacancy, signs of which were found from adsorption of acrolein. Reoxidation, therefore, has to occur by transfer of  $O^{2-}$  from the environment of U to that of Sb and reoxidation at U. The observation that the catalyst tends to decompose in the absence of oxygen leads to the conclusion that the passage of  $O^{2-}$  from U to Sb might lead to decomposition unless the reduced U is quickly regenerated by an interaction with  $O_2$ .

As has been shown by Batist, van der Heijden and Schuit (7) the isomerization over  $Bi_2O_3-MoO_3$  is a complicated process that also needs both A and B sites. Since this reaction is insufficiently understood on  $Bi_2O_3-MoO_3$ , we shall not try to discuss it any further here.

#### ACKNOWLEDGMENT

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