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On the Mechanism of *n*-Butane Oxidation to Maleic Anhydride: Oxidation in Oxygen-Stoichiometry-Controlled Conditions

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The oxidation of *n*-butane at low and high hydrocarbon concentrations is studied on a vanadium(IV)–phosphorus (1 : 1) mixed oxide in relation to the surface modifications induced by the reaction medium. The results show the formation of butenes and butadiene from *n*-butane at high *n*-butane concentrations with total consumption of the inlet oxygen; the formation of olefins from *n*-butane is not found when there is not total consumption of the oxygen or at low *n*-butane concentrations. At the conditions when the formation of olefins is a maximum, chemical analysis, EPR, and diffuse reflectance spectra show the presence in the catalyst of high amounts of V(III) together with V(IV) and the absence of V(V), whereas lower amounts of V(III) together with both V(IV) and V(V) are found, when maleic anhydride is formed. It is suggested that two redox couples operate in the maleic anhydride synthesis: (i) V(IV)–V(III) in the synthesis of olefins from *n*-butane, and (ii) V(V)–V(IV) in the synthesis of maleic anhydride from the olefins formed. At high *n*-butane concentrations and total oxygen consumption, the lower density of oxidizing sites for the second reaction limits the rate of further oxidation of butenes to maleic anhydride, thus providing evidence for their formation from *n*-butane.

INTRODUCTION

In spite of their availability and low price, the paraffins are not often utilized as feedstocks in selective oxidation reactions. One of the few examples of industrial application is the oxidation of *n*-butane to maleic anhydride, but although several patents have been published in recent years on the subject (*1*, *2*), the oxidation mechanism has not yet been investigated. Catalysts, active and selective in the oxidation of *n*-butane (vanadium–phosphorus mixed oxides based catalysts) also are active and selective in the oxidation of butenes and butadiene (*3*, *4*). In the first case, maleic anhydride and carbon oxides are the main products, whereas, in the case of butene oxidation, the yield of maleic anhydride is similar but several (about 10) products of partial oxidation are formed. Therefore, two fundamental questions arise:

—Does the oxidation of *n*-butane proceed through a particular and specific mechanism or through a preliminary dehydrogenation step to butenes followed by a mechanism analogous to that for the formation of maleic anhydride from butenes?

—Why, in the case of *n*-butane are mainly maleic anhydride and carbon oxides formed while in the case of 1-butene, a wide range of partial oxidation products are obtained?

The objective of this note is to make a contribution to the understanding of these questions.

EXPERIMENTAL

The catalytic tests were carried out in a tubular isothermal flow reactor utilizing the catalyst in the form of cylindrical pellets. A thermocouple was inserted inside the catalytic bed to control the temperature. The composition of the feed and the reaction products were analyzed with two sequential gas chromatographs on line with the reactor (*5*). The catalyst was prepared according to Katsumoto and Marquis (*6*) by reduction of V_2O_5 with isopropyl alcohol followed by the addition of *o*-H_3PO_4 (99%). The phosphorus/vanadium ratio of the cat-

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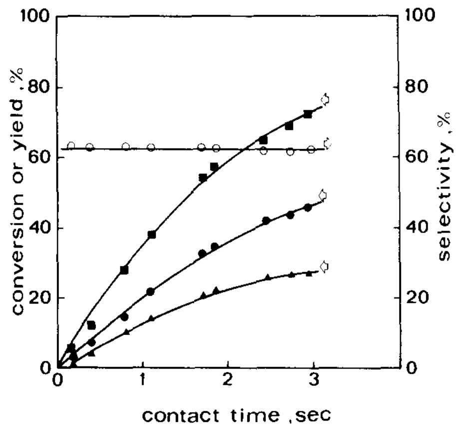


FIG. 1. Effect of contact time on the conversion (■), on the yields of maleic anhydride (●) and carbon oxides (▲), and on the selectivity in maleic anhydride (○) in the *n*-butane oxidation. Experimental conditions: temperature, 320°C; O_2/*n*-butane ratio, 15; *n*-butane concentration, 0.60 vol %.

alyst was 1.0; the catalyst is characterized by a high surface area (30 m^2/g) which allows the *n*-butane to be oxidized with high yields of maleic anhydride (about 50%) at very low temperatures (300–320°C) (*7*).

The valence state of vanadium in the catalyst was determined manganometrically according to the method of Niwa and Murakami (*8*); the titration amount of $KMnO_4$ can determine the quantity $T_1 = V^{4+} + 2V^{3+}$, where V^{4+} and V^{3+} denote the amount of the relative ions. The solution thus obtained, which contained only V^{5+} ions is used for the subsequent titration with iron(II) ammonium sulfate. Because the V^{5+} ions are reduced to V^{4+} ions in this titration, the titration amount is shown as $T_2 = V^{5+} + V^{4+} + V^{3+}$. The amount of V^{5+} ions inherently present in the initial sample can be measured independently by titration with iron(II) ammonium sulfate using another solution, $T_3 = V^{5+}$. These procedures, therefore, provide sufficient data to calculate the amounts of each ion.

Diffuse reflectance spectra were obtained with a Perkin–Elmer Model 124 spectrophotometer equipped with an integrator. ESR spectra were recorded at room temperature using a Bruker Model 200tt spectrometer operating in the X band and equipped with the standard accessories.

RESULTS

Oxidation of n-Butane and 1-Butene

Reported in Figs. 1 and 2 are the conversion and the yields in maleic anhydride and carbon oxides in the oxidation of *n*-butane versus the contact time and the oxygen/*n*-butane ratio, respectively. Only traces of acetic acid as other by-products were observed. A direct comparison between the activity of the catalyst in the oxidation of 1-butene and *n*-butane is difficult because of the easy deactivation of the catalyst in a flow of 1-butene. In fact, in order to have reproducible data of activity in the oxidation of 1-butene, it is necessary to hold the catalyst at 390°C in a flow of 1% 1-butene and air for 4 h (*7*); after this pretreatment the surface area of the catalyst decreases from 30 to 12 m^2/g. In the case of *n*-butane oxidation, the pretreatment has no effect on the surface area. To overcome this difficulty we operated in the following manner. For each temperature of analysis, a fresh amount of catalyst was used; the behavior of the catalyst was first tested in *n*-butane

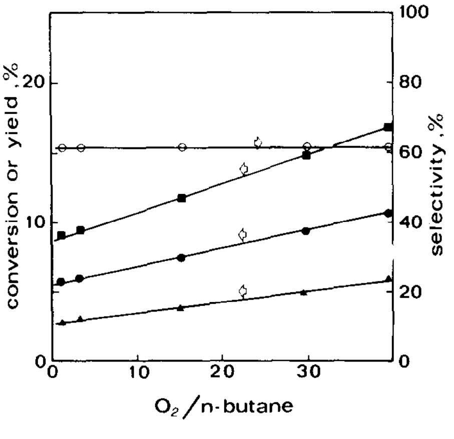


FIG. 2. Effect of O_2/*n*-butane ratio on the conversion (■), on the yields of maleic anhydride (●) and carbon oxides (▲), and on the selectivity in maleic anhydride (○) in *n*-butane oxidation. Experimental conditions: temperature, 320°C; contact time, 0.20 sec; *n*-butane concentration, 0.84 vol %.

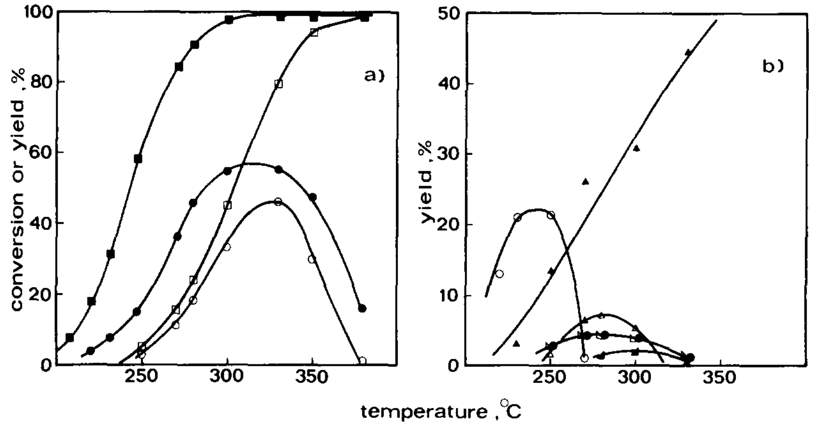


FIG. 3. (a) Comparison of the *n*-butane (open symbols) and 1-butene (full symbols) oxidation. Symbols: conversion (□■), yield of maleic anhydride (○●). Experimental conditions: hydrocarbon concentration, 0.48 vol %; oxygen concentration, 12.9 vol %; contact time, 1.36 sec; 1.9 g of catalyst. (b) By-products in the oxidation of 1-butene. Experimental conditions as in (a). Symbols: yields of butadiene (○), carbon oxides (▲), furan (△), acetaldehyde (●), methyl vinyl ketone (▷), and crotonaldehyde (▶).

oxidation, and then after switching off the hydrocarbon feed, it also was tested in the 1-butene oxidation. The catalytic data reported for 1-butene refers to the behavior 15 min after the hydrocarbon feed was switched. The results are reported in Fig. 3a; Fig. 3b shows the other by-products obtained in the 1-butene oxidation (other than carbon oxides, only traces of acetic acid were observed in the *n*-butane oxidation). In these experiments 1-butene is oxidized in a reaction temperature range about 100°C lower than that of the *n*-butane.

Oxidation of n-Butane at High Hydrocarbon Concentrations

To carry out oxidation runs at high concentrations of *n*-butane, it is necessary to decrease the oxygen concentration to under approximately 10% in order to keep outside the explosion limits. In these experimental conditions the conversion of the *n*-butane is very low (about 2%); therefore it is more useful to report the conversion of the oxygen, which is the limiting reagent.

Reported in Figs. 4 and 5 are the conversions of the oxygen and the moles/g · sec of products formed in the oxidation of *n*-butane versus the reaction temperature, and, at the temperature of maximum maleic anhydride formation, versus the oxygen concentration; for clarity, only the formations of olefins, maleic anhydride, and carbon oxides are reported in Fig. 5. In Fig. 6 the moles per hour of maleic anhydride, carbon oxides, and olefins formed versus the contact time are reported.

In Table 1 the initial activity and selectivity in the oxidation of *n*-butane at 300°C and 10% of oxygen are reported for low and high *n*-butane concentrations.

Nature of the Spent Catalyst

X-Ray diffraction patterns of the fresh catalyst and the same catalyst after the oxidation runs in different reagent concentra-

TABLE 1

Comparison of the Rate of Maleic Anhydride Formation at Low and High Hydrocarbon Concentrations[a]

n-Butane concentration (vol %)	Oxygen concentration (vol %)	$r_{\mathrm{m.a.}}$ (moles/g · sec)	Selectivity (%)
1.1	10.2	5.7×10^{-8}	55[b]
30.5	10.2	2.6×10^{-8}	79

[a] Temperature 300°C.
[b] 80% of conversion.

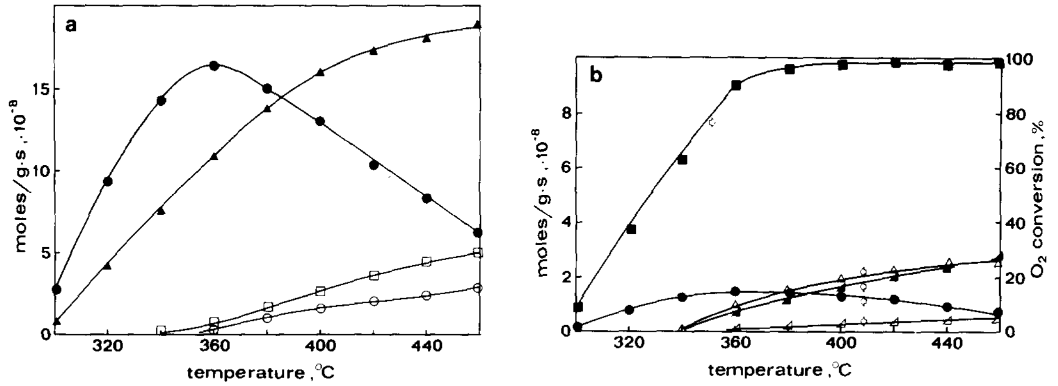


FIG. 4. Effect of the temperature on the moles/g · sec of products in *n*-butane oxidation at high paraffin concentrations. Symbols: (a) maleic anhydride (●), carbon oxides (▲), 1- and 2-butenes (□), butadiene (○). (b) Oxygen conversion (■), acetic acid (●), furan (△), crotonaldehyde (▲), and methyl vinyl ketone (▷). Experimental conditions: oxygen concentration, 10 vol %; *n*-butane concentration, 30.5 vol %; contact time, 0.95 sec; 3.5 g of catalyst.

tions are practically the same and correspond to that of the active phase for the formation of maleic anhydride (*9*, *10*).

Reported in Table 2 are the results of the chemical analyses of both the fresh catalyst and the spent catalysts.

The ESR signals of the catalysts before and after the oxidation runs at low and high *n*-butane concentrations are shown in Fig. 7. The signal of the fresh catalyst shows a large, slightly asymmetrical signal (ΔH ca. 200–250 G) which is characteristic of VO^{2+} ions with undefined and rather casual symmetries (*11*, *12*); after the catalytic tests with low *n*-butane concentrations a small but insignificant change of the *g* values is noted, however the signal broadens (ΔH ca. 450–500 G). According to Nakamura *et al.* (*13*) the broadness of the signal can be attributed to the dipolar interaction of the

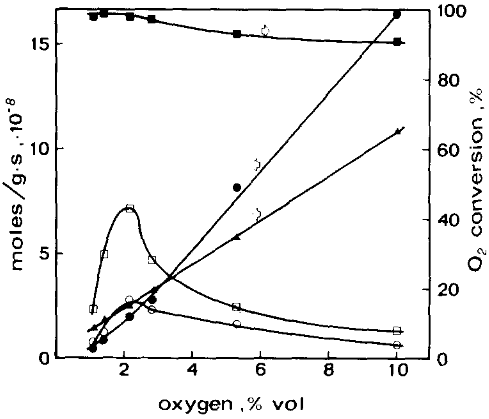


FIG. 5. Effect of oxygen on the moles/g · sec of products in *n*-butane oxidation at high paraffin concentration. Symbols: oxygen conversion (■), maleic anhydride (●), carbon oxides (▲), 1- and 2-butenes (□), and butadiene (○). Note: to facilitate reading the graph, the moles/g · sec of butenes and butadiene are twice the actual values found. Experimental conditions: temperature, 360°C; *n*-butane concentration, 30.5 vol %; contact time, 0.95 sec; 3.5 g of catalyst.

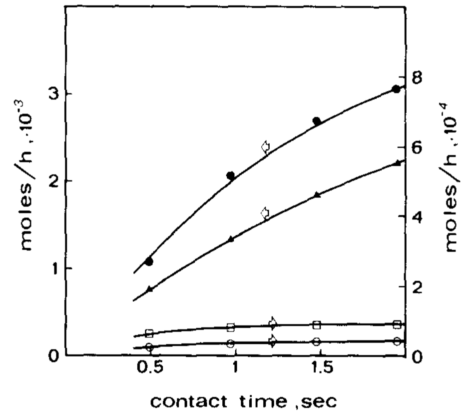


FIG. 6. Effect of contact time on the formation of maleic anhydride (●), carbon oxides (▲), 1- and 2-butenes (□), and butadiene (○) in the oxidation of *n*-butane at high paraffin concentrations. Experimental conditions: temperature, 360°C; oxygen concentration, 10 vol %; *n*-butane concentration, 30.5 vol %.

TABLE 2

Valence State of Vanadium in the Original and Spent Catalysts Determined by Chemical Analysis

n-Butane concentration (vol %)	Oxygen concentration (vol %)	V(III) (%)	V(IV) (%)	V(V) (%)
Before reaction		0	88	12
1.1	2	2	90	8
1.1	10.2	1	91	8
30.5	2	24	75	0
30.5	10.2	16	83	1

VO^{2+} ions with V^{3+} paramagnetic ions. In the catalyst used with high concentrations of *n*-butane, no ESR signal is present nevertheless chemical analysis shows the presence in the catalyst of a large amount of vanadium(IV) together with V(III) and the absence of vanadium(V) ions.

The diffuse reflectance spectra of the fresh and spent catalysts are reported in Fig. 8. The bands at about 13,000 and 16,000 cm^{-1} correspond to the *d–d* transitions of the V^{4+} ions in distorded octahedrons in $VOSO_4 \cdot 5H_2O$ (*14*), whereas the high-intensity charge transfer bands in the region 24,000–30,000 cm^{-1} are characteristic of the V^{5+} ions in octahedral coordination as in V_2O_5 (*11*, *15*); the band at 20,000 cm^{-1} can be attributed, according to King and Good (*16*), to V(III) ions in octahedral sites.

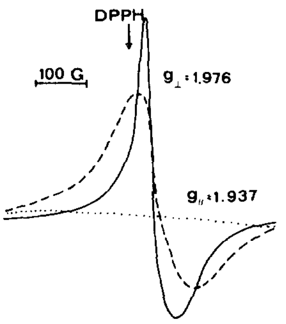


FIG. 7. Electronic spin resonance spectra of fresh and spent catalysts: (—) fresh catalyst, (---) after catalytic tests at low *n*-butane concentrations, (···) after catalytic tests at high *n*-butane concentrations.

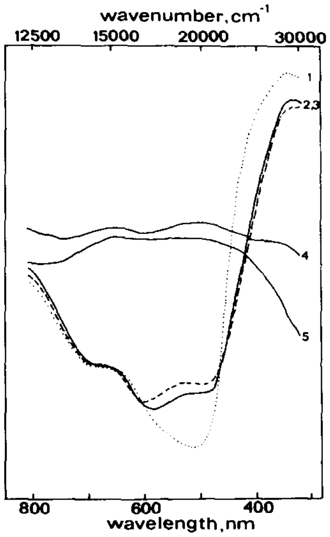


FIG. 8. Diffuse reflectance spectra of the fresh and spent catalysts: (1) fresh catalyst, (2) and (3) after catalytic tests at low *n*-butane concentration and 10 vol % of oxygen (—) and 2 vol % of oxygen (---), (4) and (5) after catalytic tests at high *n*-butane concentrations and 10% vol of oxygen (4) and 2 vol % of oxygen (5).

DISCUSSION

Comparison between 1-Butene and n-Butane

The differences observed between the two reagents are the following: (i) a large spectrum of by-products occurs with the oxidation of 1-butene; (ii) a rapid (in few hours) deactivation of the catalyst occurs during the oxidation of 1-butene with a contemporaneous decrease in the surface area (no deactivation is observed in the *n*-butane oxidation); and (iii) the initial activity is much higher in the oxidation of 1-butene than that in the *n*-butane oxidation. Assuming first-order reaction kinetics for the depletion of the two reagents (*5*, *9*, *17*), the calculated ratio of the kinetic constants ($k_{1\text{-butene}}/k_{n\text{-butane}}$) is about 40 at 300°C. For a consecutive reaction of the type,

$$n\text{-butane} \underset{r_1}{\overset{1}{\rightarrow}} \text{olefins} \underset{r_2}{\overset{2}{\rightarrow}} \text{maleic anhydride}$$

the maximum expected concentration of olefins is (*18*),

$$\frac{C_{\text{max,olefins}}}{C_{0_{n\text{-butane}}}} = \frac{k_1}{k_2}^{k_2/(k_2-k_1)} . \tag{1}$$

For an initial concentration of *n*-butane ($C_{0_{n\text{-butane}}}$) of 1 vol %, the maximum amount of olefins (as sum of the different olefins) expected is 0.04 vol %. Therefore, if the hypothesized mechanism is operating, the nondetection of olefins in the oxidation of *n*-butane could be justified only on the basis of kinetic reasons.

Oxidation at High n-Butane Concentrations

We carried out oxidation runs at high *n*-butane concentrations (i) in order to increase the detectability of the intermediate in the oxidation of *n*-butane to maleic anhydride, according to Eq. (1), and to see whether the vanadium–phosphorus oxide catalysts are able to dehydrogenate the paraffin, and (ii) for the purpose of exploring possibility of synthesizing maleic anhydride at high *n*-butane concentrations with an eventual recycling of the reagent, because at low *n*-butane concentrations selectivities and productivities are low. It can be seen from the data in Table 1 that the selectivity in maleic anhydride is higher when the oxidation is carried out at high *n*-butane concentrations than when it is carried out at low *n*-butane concentrations. However, in contrast to the results obtained in the catalytic tests at low hydrocarbon concentrations, high amounts of butenes and butadiene as well as of other by-products present in the direct oxidation of olefins are obtained both by increasing the reaction temperature or by decreasing the oxygen concentration. This occurs in both cases when the oxygen conversion is 100%; furthermore an increase in the formation of the olefins cannot be detected at lower contact times (Fig. 6) and the selectivity in maleic anhydride is approximately constant in the range examined. This suggests that the total consumption of the oxygen is the only key factor in obtaining modifications in the selectivity in maleic anhydride formation and for detecting the formation of olefins.

These results show that vanadium–phosphorus oxides are able to dehydrogenate the *n*-butane to butenes and butadiene; these olefins react further to form all the products of partial oxidation found in the case of 1-butene oxidation on the same catalyst. The question is whether, in the catalytic runs at high *n*-butane and total consumption of the oxygen, the mechanism of *n*-butane oxidation changes or the relative ratio between the two rates of olefins and maleic anhydride formation (r_1/r_2) changes. Figure 4 shows that when the reaction temperature is increased, the olefins are detected only when the oxygen conversion reaches 100%; chemical and spectroscopic analyses on the spent catalyst show that a large amount of V(III) is present on the bulk and surface of the catalyst. Furthermore, the initial activity at high *n*-butane concentrations is lower than at low concentrations indicating that the *n*-butane causes a deactivation of the catalyst. Therefore, in order to interpret the behavior of the catalyst at high concentrations of *n*-butane and to learn the reasons for the formation of butenes in oxygen deficient conditions, the nature of the spent catalyst must be analyzed.

Nature of the Spent Catalyst

X-Ray diffraction patterns of fresh and spent catalysts in the different conditions of *n*-butane and oxygen concentrations are practically the same and correspond to that of the so-called B-phase (*19*) (patented active phase), with only some slight variations in the relative intensities of the lines.

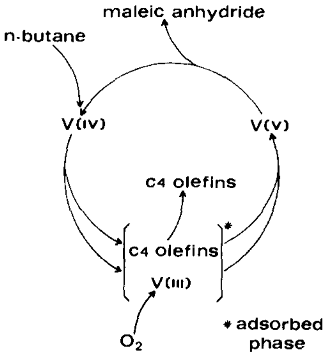
The fresh catalyst is a vanadium(IV) compound with 12% vanadium(V). Diffuse reflectance spectra showed the presence of both V(IV) and V(V) absorption at the surface. In the spent catalyst which was used at low *n*-butane concentrations and at either low or high oxygen concentrations, only a slight reduction of the V(V) content occurred, with the formation of a small amount (about 1–2%) of vanadium(III). Diffuse reflectance spectra showed the presence, at the surface, of the V(III) species in addition to the V(IV) and V(V) species. The broadness of the ESR signal of vanadium(IV) as compared to that of the fresh catalyst also was attributed to the interaction of V(IV) with V(III) ions. In the spent catalyst, which was used at high concentrations of *n*-butane, chemical analysis showed the presence of a large amount of vanadium(III), but no V(V); the amount of V(III) increases in the tests at low oxygen concentration. No signal was observed in the ESR spectra, testifying to the strong interaction of V(IV) with V(III). The diffuse reflectance spectra confirm the presence of higher amounts of surface V(III) ions and the presence of very small amounts of V(V) ions.

Mechanism of n-Butane Oxidation

Callahan and Grasselli (*20*) originated the concept of "density of oxidizing sites" as a tool to modify the selectivity in reactions of selective oxidation. They showed that it is possible to decrease the formation of carbon oxides, increasing the selectivity in acrolein by the partial reduction of a metal oxide (CuO). We think that a similar effect is present in our case: at high *n*-butane concentrations and total oxygen conversion, the k_1/k_2 ratio changes due to the surface reduction induced by the reaction with the *n*-butane. In fact, the results obtained suggest the hypothesis that different redox couples are involved in the reactions: (i) a redox couple V(IV)–V(III) in the dehydrogenative oxidation of *n*-butane to olefins; and (ii) a redox couple V(V)–V(IV) necessary for the synthesis of maleic anhydride from the olefins. The importance of the redox couple V(V)–V(IV) in the synthesis of maleic anhydride from 1-butene also has been suggested previously by other authors (*10, 13, 21*). This mechanism agrees with previous results in 1-butene oxidation on vanadium–phosphorus oxides (*22, 23*); butadiene is formed in pulse tests, in the absence of gaseous oxygen, on a catalyst of vanadium(IV) only, whereas maleic anhydride is formed on a catalyst which contains both V(IV) and V(V). At high *n*-butane concentrations the relative ratio of the V(III), V(IV), and V(V) ions changes and therefore, according to the suggested mechanism, the k_1/k_2 ratio increases and thus it is possible to show the formation of olefins.

The mechanism of *n*-butane oxidation can now be interpreted as follows: olefins are formed from *n*-butane and when no oxidizing sites are available in the neighboring areas (due to the higher degree of surface reduction), the olefins desorb without further reaction; when oxidizing sites are available, the olefins react very quickly to give maleic anhydride or carbon oxides. This interpretation is in agreement with the model of active sites proposed recently by Ziółkowski (*24*) in which, based on the catalytic anisotropic properties of oxides, it was hypothesized that the selective formation of various oxygen-containing reaction products depends on the number and configuration of active oxygen in the nearest vicinity of the adsorption site. It is possible to discuss the results of Figs. 4 and 5 on the basis of this proposed mechanism. Increasing the temperature (Fig. 4) causes a greater increase in the rate of the parallel reaction of carbon oxides formation than that of maleic anhydride formation (*25*). Since, for temperatures higher than 360°C, total consumption of the oxygen occurs during the reaction, the higher rate of carbon oxides formation limits the number of oxidizing sites for the synthesis of maleic anhydride and therefore, it is possible to detect the formation of the olefins from *n*-butane. Decreasing the oxygen concentration at 360°C (temperature of maximum formation of maleic anhydride) (Fig. 5), decreases the number of oxidizing sites available for the formation of both carbon oxides and maleic anhydride and thus it is possible to show the formation of olefins. At low *n*-butane concentrations, the density of oxidizing sites is higher and the olefins formed react very quickly to form maleic anhydride; under this condition, the oxygen concentration does not change drastically the relative ratio of surface vanadium ions and thus it is not possible to isolate the active sites for the dehydrogenation of *n*-butane from those necessary to oxidize the olefins.

We believe that the mechanism of oxidation is similar at low and high *n*-butane concentrations, but that the distribution of active sites under the two conditions is different. Therefore it is possible to suggest the following mechanism for the synthesis of maleic anhydride from *n*-butane:



SCHEME 1. General scheme of the *n*-butane oxidation to maleic anhydride on vanadium–phosphorus oxide catalysts.

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