Mechanism of Phthalic Anhydride Formation in the Oxidation of *n*-Pentane on a Vanadium–Phosphorus Oxide Catalyst

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Received June 30, 2005

Abstract—The reaction paths of product formation in the partial oxidation of *n*-pentane on vanadium–phosphorus oxide (VPO) and VPO–Bi catalysts are considered. The condensed products of *n*-pentane oxidation were analyzed by chromatography–mass spectrometry, and the presence of C_4 rather than C_5 unsaturated hydrocarbons was detected. It was found that the concentration of phthalic anhydride in the products increased upon the addition of C_4 olefins and butadiene to the *n*-pentane–air reaction mixture. With the use of a system with two in-series reactors, it was found that the addition of butadiene to a flow of *n*-butane oxidation products (maleic anhydride, CO, and CO_2) resulted in the formation of phthalic anhydride. The oxidation of 1-butanol was studied, and butene and butadiene were found to be the primary products of reaction; at a higher temperature, maleic anhydride and then phthalic anhydride were formed. The experimental results supported the reaction scheme according to which the activation of *n*-pentane occurred with the elimination of a methyl group and the formation of C_4 unsaturated hydrocarbons. The oxidation of these latter led to the formation of maleic anhydride. The Diels–Alder reaction between maleic anhydride and C_4 unsaturated hydrocarbons is the main path of phthalic anhydride formation.

DOI: 10.1134/S0023158406060012

INTRODUCTION

Progress achieved in the development of *n*-butane oxidation to maleic anhydride, which substituted for benzene oxidation in actual practice, is responsible for studies on the partial oxidation of other paraffin hydrocarbons. One of these reactions is *n*-pentane oxidation, which occurs in the presence of vanadium–phosphorus oxide (VPO) catalysts with the formation of the following three anhydrides: phthalic anhydride, maleic anhydride, and citraconic anhydride. The formation of phthalic anhydride, which contains a greater number of carbon atoms than that in the parent paraffin molecule, is of particular interest.

Promising results were obtained in the early studies of *n*-pentane oxidation on VPO catalysts [1–3], and they demonstrated the possibility of reaching a high yield of phthalic anhydride. More recently, it was found that the main product of *n*-pentane partial oxidation on VPO and other catalysts is maleic anhydride, whose amount in the products is greater than the concentration of phthalic anhydride [4–10]. Calestani et al. [11, 12] found an effect of the surface state of a VPO catalyst on the ratio between these anhydrides, whereas Cavani et al. [13] attempted to increase the yield of phthalic anhydride by adding iron and cobalt to a VPO catalyst; generally, this attempt was unsuccessful. However, Zazhigalov [14] found that a bismuth additive increased the yield of phthalic anhydride. Zazhigalov et al. [7, 8]

found that methylmaleic (citraconic) anhydride was formed along with the above anhydrides in the oxidation of *n*-pentane on VPO catalysts. The formation of citraconic anhydride was also confirmed by published data [9, 14, 15]. The mechanism of product formation in the partial oxidation of *n*-pentane was discussed previously [2, 7, 9, 10, 14–19]; however, there is no agreement on this subject. Centi et al. [3] proposed a reaction scheme for the formation of *n*-pentane oxidation products (Fig. 1a) via paraffin dehydrogenation with pentadiene cyclization; however, it is inconsistent with published experimental data. Another reaction scheme of product formation was proposed for the oxidation of *n*-pentane on VPO catalysts (Fig. 1b) [14, 26]; however, some of the steps in this reaction scheme should be supported experimentally. In this context, we performed an integrated study of the mechanism of product formation in the oxidation of *n*-pentane on VPO catalysts.

EXPERIMENTAL

The mechanism of *n*-pentane conversion was studied using VPO and VPO–Bi catalysts (P/V = 1.15 and Bi/V = 0.1) synthesized in an *n*-butanol solution according to a procedure described elsewhere [14]. According to XRD data, the synthesized catalysts contained a $VOHPO_4 \cdot 0.5H_2O$ phase and, additionally, $BiPO_4$ in the case of the VPO–Bi sample. The samples were preactivated in the reaction of *n*-butane oxidation
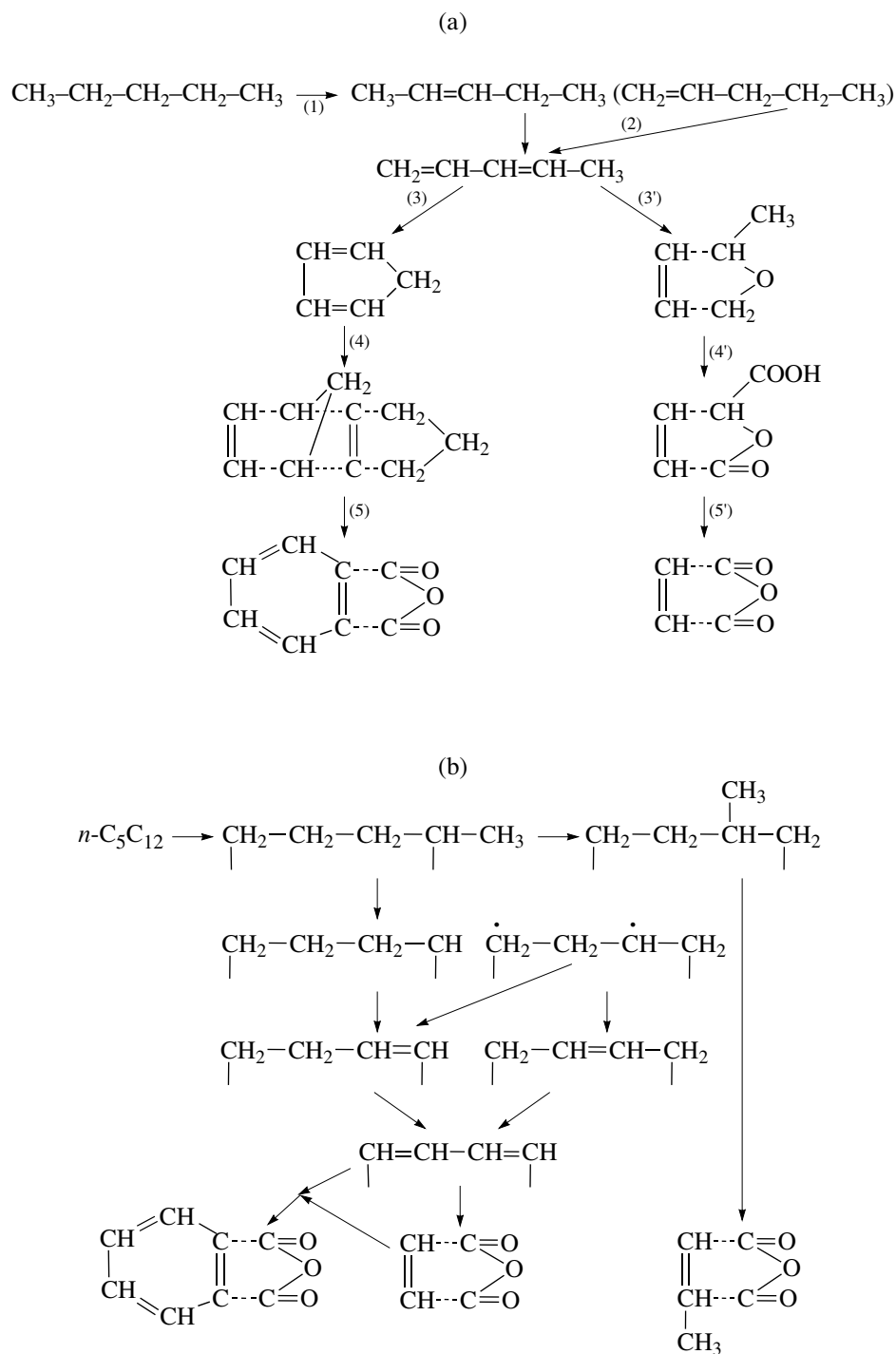
(a)

(b)

Fig. 1. *n*-Pentane oxidation schemes proposed by (a) Centi et al. [3] and (b) Zazhigalov [14].

(1.7 vol % in air) until steady-state conditions were reached in this process (415°C, $X_{C_4H_{10}} = 88\%$, and $S_{\text{maleic anhydride}} = 61\%$ for VPO or 405°C, $X_{C_4H_{10}} = 92\%$, and $S_{\text{maleic anhydride}} = 64\%$ for VPO–Bi). After the activation, the catalysts comprised a $(VO)_2P_2O_7$ phase (a $BiPO_4$ phase was also present in the case of VPO–Bi)

with the most intense reflections at $d = 0.388$, 0.313, 0.298, and 0.194 nm.

The surface properties of the samples were studied by XPS on a VG ESCA-3 spectrometer. The measurement and processing of the spectra were performed on a PC using the ESCA-3 program. The C1*s* line

(284.8 eV) served as a reference for the determination of binding energies.

Catalytic experiments on *n*-pentane oxidation were performed in a stainless steel reactor 6 mm in i.d. The catalyst (0.25–0.50 mm) loading was 0.5 cm³. The flow rates of reaction mixtures (26–75 cm³/min) were regulated using mass flow meters from ERG. The following working mixtures, as well as pure butadiene-1,3, were used in this study: (**A**) *n*-pentane (1.6 vol %)–air, (**B**) *n*-pentane (1.56 vol %)–butene-1 (1.05 vol %)–air, (**C**) *n*-pentane (1.62 vol %)–butene-2 (0.98 vol %)–air, (**D**) *n*-pentane (1.58 vol %)–butadiene-1,3 (0.96 vol %)–air, (**E**) 1-butanol (0.98 vol %)–air, and (**F**) *n*-butane (1.7 vol %)–air. The working mixtures were prepared in advance and stored in 40-l steel gas cylinders at a pressure of 50 atm. The following reagents were used: *n*-pentane (99%, Fluka), butene-1 (99%, Aldrich), butene-2 (99% *cis*- and *trans*-butene mixture, Aldrich), butadiene-1,3 (99.5%, Fluka), *n*-butane (98.5%, grade A), 1-butanol (analytical grade), and helium (high-purity grade). 1-Butanol was supplied by passing a flow of air through a trap with the alcohol thermostated at 50°C.

We designed a special setup (Fig. 2) of two in-series reactors in order to study the possibility of phthalic anhydride formation by the Diels–Alder reaction. The temperature in the reactors was regulated independently. Mixture **F** was passed through both of the reactors at a flow rate of 98–99 ml/min. The first reactor was loaded with 0.5 cm³ of the VPO–Bi catalyst, and the second reactor was also loaded with 0.5 cm³ of quartz glass or a catalyst. Helium or butadiene-1,3 was additionally supplied at a flow rate of 1–2 ml/min at the inlet of the second reactor.

The online analysis of starting mixtures and reaction products was performed using thermostated sampling valves (150–160°C) on two Chrom 5 gas chromatographs with PC recording and processing. Analysis for O_2 and CO was performed on a column packed with NaX molecular sieves (2-m column; $T = 10–11°C$; thermal-conductivity detector (TCD)), whereas analysis for CO_2 and hydrocarbons was performed on a column with KSK-2.5 silica gel (3-m column; $T = 50–150°C$; temperature-programmed conditions; TCD). The carrier-gas (He) flow rate through the columns was 80 ml/min. A column with F-50 (5 wt %) on Chromosorb P (2 m; $T = 100–220°C$; temperature-programmed conditions; flame-ionization detector (FID)) was used for the determination of the resulting oxygen-containing products, whereas the separation of hydrocarbons was performed on a column packed with dimethylsulfolane (15 wt %) on Chromosorb A (2 m; $T = 25°C$; FID). The carrier-gas (He) flow rate was 50 ml/min.

The use of a condenser (after sampling valves) allowed us to condense additionally the products and analyze them after thawing or dissolving in acetonitrile by gas chromatography–mass spectrometry (GC–MS) (Varian 3400 + Incos-50 Finnigan). This analysis was used at regular intervals (after the accumulation of
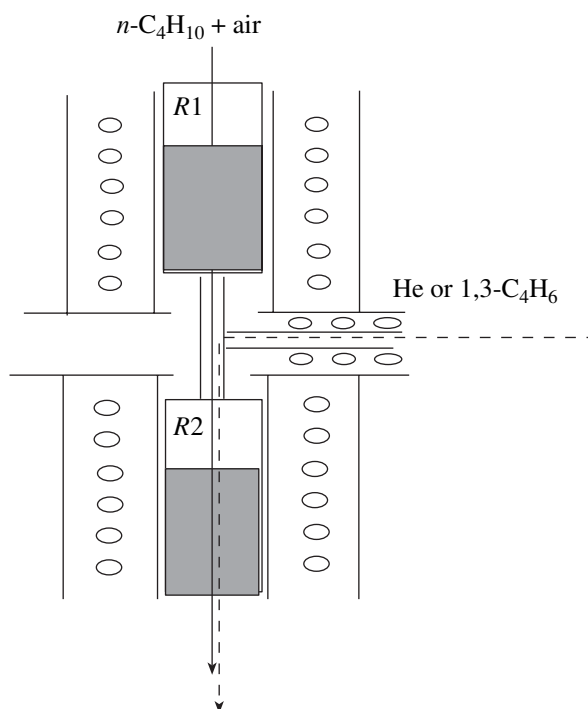
Fig. 2. Schematic diagram of the catalytic setup (R1 and R2 are the first and second catalytic reactors, respectively).

products under constant reaction conditions for 5–6 h) to determine substances whose concentrations were lower than the sensitivity of flow GC analysis.

RESULTS AND DISCUSSION

The reaction scheme (Fig. 1a) proposed by Centi et al. [3] implies the formation of C_5 unsaturated hydrocarbons (pentenes and pentadiene) as primary intermediate products in the oxidation of *n*-pentane. Note that none of these products was detected in the study of the reaction on VPO catalysts with the use of GC analysis. They were also not detected by the temporal analysis of products (TAP) with the use of mass spectrometry in a study of *n*-pentane conversion [18].

We performed the accumulation of *n*-pentane oxidation products followed by GC–MS analysis. Figure 3 shows mass spectra for the fragments of product chromatograms. Peaks with $m/z = 55, 67$, and 70, which are most intense for pentenes and pentadiene, are absent from the spectra (Fig. 3a). At the same time, the mass spectrum exhibits peaks with $m/z = 27, 29, 39, 41, 56$, and 54, which are characteristic of C_4 unsaturated hydrocarbons. The peak with $m/z = 68$ can be due to the presence of citraconic anhydride (maximum intensities at $m/z = 39, 68$, and 40) or furan ($m/z = 68$ and 39) in the products. Thus, the experimental results allowed us to conclude that C_4 rather than C_5 unsaturated hydrocarbons were present in *n*-pentane oxidation products;
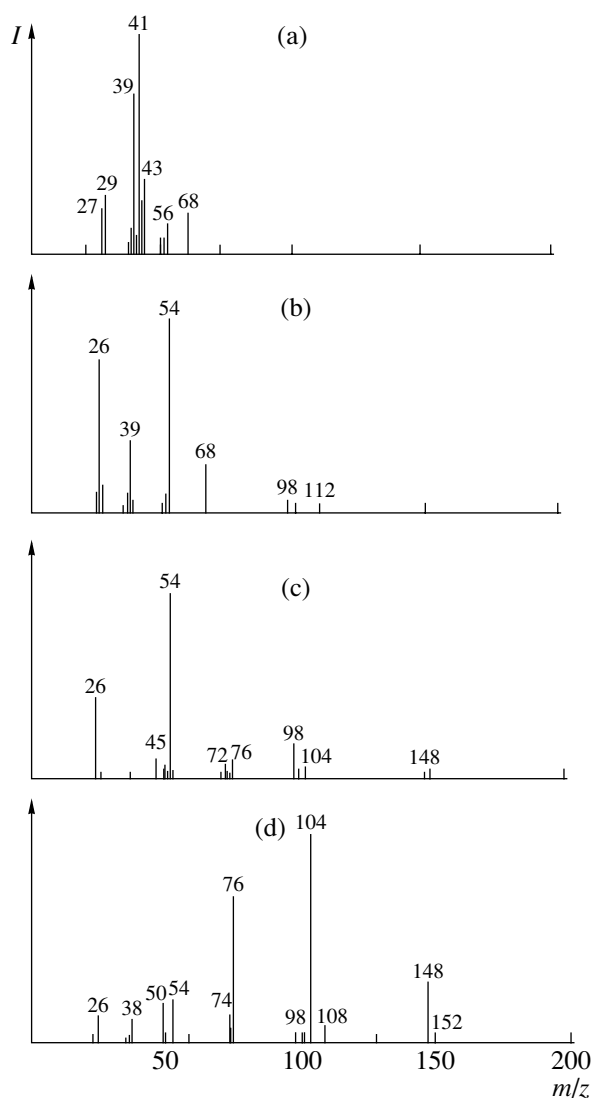
Fig. 3. Mass spectra of *n*-pentane oxidation products (analysis of chromatogram fragments).

these results are consistent with the proposed reaction scheme (Fig. 1b).

Published explanations for the absence of C_5 unsaturated hydrocarbons because of high rates of their conversion into phthalic anhydride and maleic anhydride were not supported by experimental data from other publications (see table). As can be seen in the table, the selectivity of phthalic anhydride formation from pentene-1, pentadiene, and cyclopentadiene was negligibly small, whereas it was close to 40% in the case of pentane; in all cases, hydrocarbon conversions were similar. The selectivity was also low in the oxidation of pentene-2. Note that the selectivity to maleic anhydride in the oxidation of C_5 olefins was also much lower than that in the oxidation of pentane. At the same time, C_4 olefins were oxidized to maleic anhydride with high selectivities even at considerable conversions (see table).

Centi et al. [3] proposed rather exotic compounds as intermediate products in the reaction scheme of maleic anhydride formation from pentadiene (Fig. 1a). More simply, the process could be conceived to occur through methylfuran and 2-furaldehyde (furfurol), which were very selectively oxidized to maleic anhydride (see table). However, note that peaks with $m/z = 82$ and 96, which are most characteristic of these compounds, were absent from mass spectra (Fig. 3).

An analysis of mass spectra for the second and third fragments of the chromatogram (Figs. 3b, 3c) demonstrated the presence of peaks characteristic of maleic anhydride ($m/z = 54$, 26, and 98), citraconic anhydride ($m/z = 39$, 68, and 112), and phthalic anhydride ($m/z = 104$, 76, and 148). Peaks with $m/z = 72$ and 45 can belong to maleic acid. In a mass spectrum for the fourth fragment of the chromatogram, the most important peaks are due to phthalic anhydride ($m/z = 104$, 76, 148, 50, 74, and 38). Peaks with $m/z = 54$, 26, and 98 characterize the presence of maleic anhydride, whereas peaks with $m/z = 108$ and 152 can belong to tetrahydrophthalic anhydride.

Thus, the experimental results obtained in this work and published data count in favor of the reaction scheme proposed for *n*-pentane oxidation (Fig. 1b) through the intermediate formation of C_4 rather than C_5 unsaturated hydrocarbons. The presence of C_4 unsaturated hydrocarbons and, likely, furan (an intermediate product in the oxidation of butenes to maleic anhydride [27]) suggests the reaction path of maleic anhydride formation in the oxidation of *n*-pentane. It is well known that the oxidation of C_4 olefins on VPO catalysts occurs at a high rate and with high selectivity. It is our opinion that phthalic anhydride is formed by the Diels–Alder reaction between maleic anhydride and a surface diolefinic compound. It is well known [28] that the Diels–Alder reaction with the participation of butadiene occurs in the forward direction at 250–300°C (i.e., under reaction conditions of *n*-pentane oxidation), and it is catalyzed in the presence of acid sites. The reaction between maleic anhydride and olefin-like surface structures, which leads to the formation of tetrahydrophthalic anhydride, also cannot be excluded. As well as hexahydrophthalic anhydride, tetrahydrophthalic anhydride is selectively oxidized with the formation of phthalic anhydride (see table). Note that, in the Diels–Alder reaction between two cyclopentadienes, which was proposed by Centi et al. [3] (Step (4) in Fig. 1a), equilibrium is shifted toward the parent compounds at temperatures higher than 80°C [28]. Because of this, the occurrence of this reaction at the temperatures of *n*-pentane oxidation on VPO catalysts is improbable. According to the reaction scheme in Fig. 1b, the formation of phthalic anhydride by the Diels–Alder reaction in the oxidation of *n*-pentane is limited because of a low steady-state concentration of surface C_4 olefin structures, which are rapidly oxidized to maleic anhydride. Because of this, an increase in the concentration of these structures by adding them to the reaction mixture

Published data on the oxidation of *n*-pentane and possible intermediate compounds

Substrate	Oxidation parameters*						References
	T_r, °C	C_{HC}, vol %	V, g s ml^{-1}	X, %	$S_{phthalic\ anhydride}$, %	$S_{maleic\ anhydride}$, %	
n-Pentane	318	2.2	1.1	20	37	13	[20]
1-Pentene	303	2.2	1.1	20	0	8	[3, 20]
1,3-Pentadiene	290	2.2	1.1	20	2	14	[3, 20]
Cyclopentadiene	285	2.2	1.1	20	0	10	[3]
n-Pentane	340	1.0	1.0	25	40	35	[15]
Pentene-2	340	1.0	1.0	35	13	16	[15]
Butene-1	440	1.5	2.4	50	**	70	[21]
Butadiene	440	1.5	2.4	50	**	58	[21]
Butene-1	360	1.5	2.4	20	**	15	[22]
Butadiene	360	1.5	2.4	21	**	37	[22]
Butene-1	400	1.3	1.5	95	**	23	[23]
cis-Butene-2	400	1.3	1.5	95	**	21	[23]
trans-Butene-2	400	1.3	1.5	95	**	36	[23]
Hexahydrophthalic anhydride	305	2.2	1.1	20	65	5	[3]
Tetrahydrophthalic anhydride	330	2.2	1.0	72	52	4	[24]
Methylfuran	330	1.8	0.9	94	**	43	[25]
Furfurol	330	1.8	0.9	95	**	59	[25]

  * T_r is the reaction temperature; C_{HC} is the concentration of the oxidized substance; V is the space velocity; X is the conversion; and $S_{phthalic\ anhydride}$ or $S_{maleic\ anhydride}$ is the selectivity to phthalic anhydride or maleic anhydride, respectively.
 ** Not determined.

will increase the concentration of the resulting phthalic anhydride.

Figure 4 shows the results of *n*-pentane oxidation obtained upon the introduction of C_4 olefins and butadiene into the reaction mixture. Indeed, as can be seen in Fig. 4, the replacement of a reaction mixture containing *n*-pentane in air (**A**) by a mixture with 1-C_4H_8 added (**B**) resulted in an increase in the concentration of phthalic anhydride in the reaction products. Simultaneously, an increase in the concentration of maleic anhydride was observed; this was due to olefin oxidation to maleic anhydride. A change to the initial reaction mixture (**A**) restored the initial concentrations of phthalic anhydride and maleic anhydride in the products. The supply of mixture **C** containing *n*-C_5H_{12} and 2-C_4H_8 also resulted in an increase in the concentrations of phthalic anhydride and maleic anhydride. Note that, in this case, the increase in the maleic anhydride concentration was somewhat greater than that in the previous case; correspondingly, the concentration of phthalic anhydride increased to a lesser extent. The greatest increase in the phthalic anhydride concentration in the reaction products was detected with the use of a mixture containing butadiene-1,3 as an additional constituent (**D**). In general, the results obtained in this study support our hypothesis on the possibility of an increasing phthalic anhydride concentration in the products upon adding C_4 olefins to the reaction mix-

ture. This hypothesis was based on the reaction scheme proposed for *n*-pentane oxidation (Fig. 1b). According to this reaction scheme, phthalic anhydride is formed in the Diels–Alder reaction between maleic anhydride and C_4 unsaturated hydrocarbons, the low steady-state concentration of which limits the process. Taking into account the above, the experimental data provide support to this reaction scheme for C_5H_{12} conversion and, in particular, to the mechanism of phthalic anhydride formation.

On the other hand, it is believed that an increase in the concentration of phthalic anhydride upon the addition of C_4 unsaturated hydrocarbons to an *n*-C_5H_{12}–air reaction mixture can be due to a change in the steady state of the catalyst surface as a result of the C_4 oxidation reaction. This assumption is based on the XPS data on the surface state of the VPO catalyst after its use in the reactions of *n*-pentane and butene-1 oxidation. It was found that the binding energy of V2*p* electrons on the catalyst surface was 517.1 eV after performing the former reaction, and the oxidation number of vanadium was equal to +4.03, as estimated using an equation from [29]. At the same time, after the oxidation of the olefin, the value of E_b for V2*p* electrons was higher (517.9 eV), and the oxidation number of vanadium was equal to +4.67. This is consistent with previous data [22, 30, 31], which indicated that the $(V^{4+}O)_2P_2O_7$ phase is more selective in the partial oxidation reaction of a par-
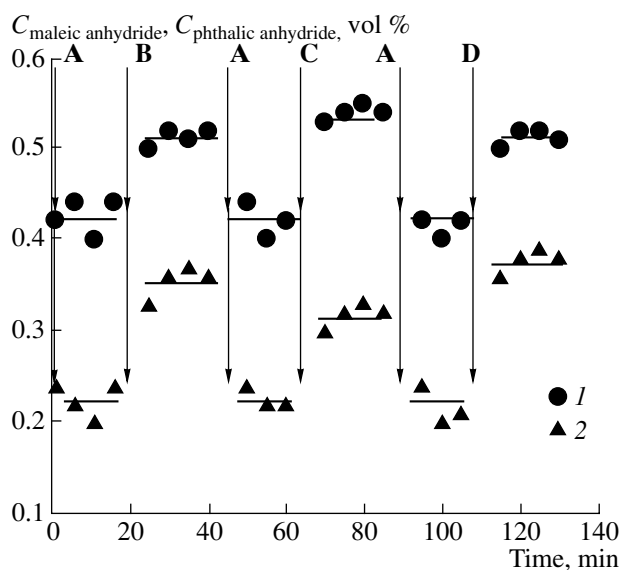
Fig. 4. Concentrations of products ((*1*) maleic anhydride and (*2*) phthalic anhydride) in the oxidation of mixtures containing (**A**) C_5H_{12} + air, (**B**) C_5H_{12} + 1-C_4H_8 + air, (**C**) C_5H_{12} + 2-C_4H_8 + air, and (**D**) C_5H_{12} + C_4H_6 + air.
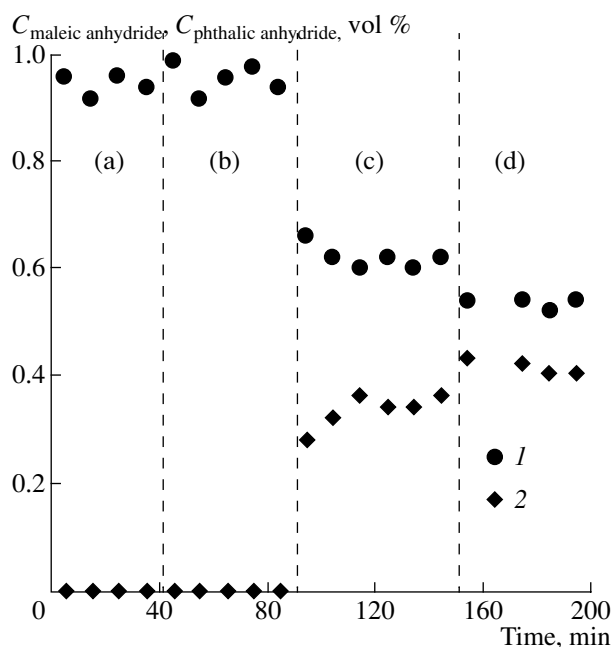

Fig. 5. Concentrations of products ((*1*) maleic anhydride and (*2*) phthalic anhydride) at the outlet of the setup with two reactors (Fig. 2): (a) a mixture of C_4H_{10} + air was passed through R1 and R2, (b) a flow of He (1–2 cm³/min) was added to the inlet of R2, (c) the replacement of a flow of He by a flow of C_4H_6 in R2 (the VPO catalyst in R2), and (d) analogously to (c) with the VPO–Bi catalyst in R2.

affin (*n*-butane), whereas high selectivity to maleic anhydride was reached in the oxidation of 1- and 2-butenes in the presence of the $V^{5+}OPO_4$ phase.

In this context, we performed studies in a setup of two in-series reactors (Fig. 2). The selective oxidation

of *n*-butane to maleic anhydride occurred in the first of the reactors at $T = 405°C$ in the presence of the VPO–Bi catalyst. In the second reactor, the reaction (oxidation of *n*-butane or further oxidation of maleic anhydride) did not occur at 250°C, as evidenced by the constant concentrations of products at the outlet of the setup upon loading quartz glass or a catalyst into this reactor (Fig. 5). In special experiments, we also found that, under the specified conditions in the presence of the VPO or VPO–Bi catalyst, the reaction of butadiene conversion almost did not occur in the second reactor (air was passed through both of the reactors at a flow rate of 98 ml/min, and C_4H_6 was supplied at the inlet of the second reactor at a flow rate of 1–2 ml/min). Figure 5 shows that the replacement of a flow of helium at the inlet of the second reactor by an analogous flow of buta-diene-1,3 resulted in the appearance of phthalic anhy-dride, which was absent previously, in the reaction products. In this case, note that the amount of the result-ing phthalic anhydride was greater with the VPO–Bi catalyst loaded in the second reactor than that with the VPO sample. Attention is drawn to the fact that the con-centration of phthalic anhydride is equivalent to the dif-ference in the amounts of maleic anhydride before and after the addition of C_4H_6 to the reaction mixture for both of the catalysts used in the second reactor.

Thus, the above results unambiguously suggest that, on the addition of C_4 unsaturated hydrocarbons to an *n*-pentane–air reaction mixture, the Diels–Alder reac-tion between the hydrocarbons and maleic anhydride, which is formed by the oxidation of *n*-C_5H_{12}, rather than a change in the steady state of the catalyst surface is responsible for an increase in the formation of phthalic anhydride. These results provide support to the reaction path proposed for the formation of phthalic anhydride in *n*-pentane oxidation (Fig. 1b) and to the hypothesis that this process is limited by a low steady-state concentration of surface olefinic or diolefinic structures.

The CO_2/CO ratio in the oxidation products is another aspect of interest. Data given in Fig. 6 indicate that the amount of CO formed in the oxidation of *n*-butane on the VPO catalyst over the entire range of reaction temperatures was greater than the amount of CO_2. This result is also consistent with published data. In this case, the CO_2/CO ratio varied over the range 0.68–0.88. In the oxidation of *n*-pentane, the amount of CO_2 in the products was always greater than the CO content, and the CO_2/CO ratio varied over the range 1.24–1.42. An analogous ratio of $CO_2/CO = 1.18–1.44$ was also observed in the oxidation of *n*-butene on the VPO catalyst. The same values of this ratio were also found in the oxidation of butenes and butadiene (for example, see [30, 32–34]). In our opinion, these results can also indirectly evidence the occurrence of *n*-pentane oxidation through the intermediate forma-tion of C_4 unsaturated hydrocarbons.

The analysis of published data raises the question: Why was phthalic anhydride not detected in the majority of studies devoted to the partial oxidation of butenes? The only exception is a publication by Krylova et al. [35], who detected phthalic anhydride and phthalic acid in the products using liquid chromatography and mass spectrometry and hypothesized that these compounds resulted from the Diels–Alder reaction with the participation of butadiene and butenes.

In our opinion, this can be due to a few reasons: (1) This product cannot be determined in principle with the use of online chromatographic procedures for product analysis or the peak of phthalic anhydride was strongly diffuse because of a long retention time. This was evidenced by a survey of chromatographic methods of analysis [36]. (2) Because of different steady states on the surface of the VPO catalyst in the oxidation of butenes and n-pentane (see the above XPS data), the concentration of phthalic anhydride formed in the oxidation of C_4 unsaturated hydrocarbons was very low and it could be detected only after accumulating the products, as performed by Krylova et al. [35]. (3) The molecular and electronic structures of the olefin fragments formed immediately on the catalyst surface in the course of oxidation were different from those of the fragments of butene adsorbed from the reaction mixture; this was responsible for a low concentration of phthalic anhydride in the reaction of butene oxidation on VPO catalysts.

We also performed a study with the accumulation of the products of butene-1 and n-butane oxidation on the VPO catalyst followed by GC–MS analysis after dissolving the products in acetonitrile. Figure 7 shows the results of this study. As can be seen in Fig. 7, the products of butene-1 oxidation exhibited peaks that can characterize the presence of maleic anhydride ($m/z =$ 54, 26, 98, and 25), maleic acid (72, 45, 26, 27, and 54), phthalic anhydride (104, 76, 148, and 50), and phthalic acid (105, 122, 104, and 76). The presence of crotonaldehyde (41, 70, 39, and 69), methyl vinyl ketone (55, 43, 70, and 27), and furan (68, 39, 38, and 40) in small amounts was possible. The mass spectrum of n-butane oxidation products exhibited peaks characteristic of maleic anhydride (54, 26, 98, 25, 53, and 28) and maleic acid (72, 45, 26, 27, 54, 55, and 104). Chromatographic analysis data suggest that acrylic acid and acetic acid ($m/z = 43, 45, 60, 15$, and 42) were also present in small amounts; however, the main peaks of acrylic acid (27, 55, 72, 26, and 45) interfered with the peaks of the above compounds.

Thus, the experimental results supported the formation of phthalic anhydride in the oxidation of butenes; however, phthalic anhydride was formed in small amounts. In turn, a difference in the oxidation products of n-butane and butene-1 should be noted, which casts some doubt on the repeatedly proposed mechanism of paraffin oxidation through dehydrogenation.
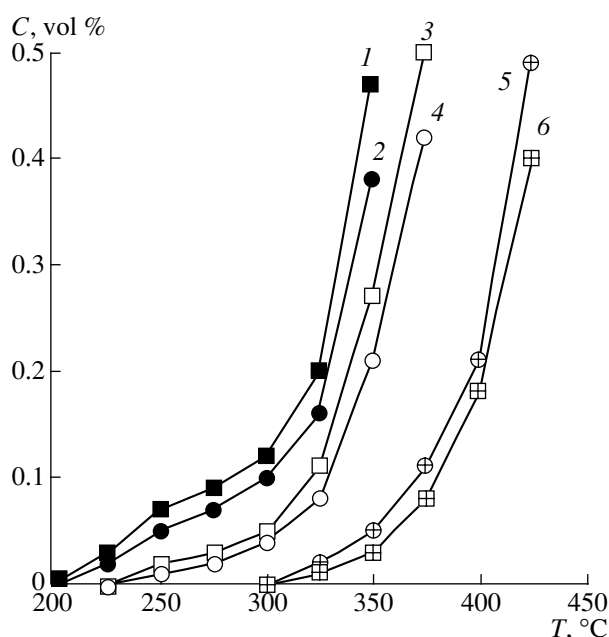
Fig. 6. The temperature dependence of the concentrations of (2, 4, 5) CO and (1, 3, 6) CO_2 in the oxidation products of (1, 2) n-C_5H_{12}, (3, 4) 1-C_4H_8, and (5, 6) n-C_4H_{10}.
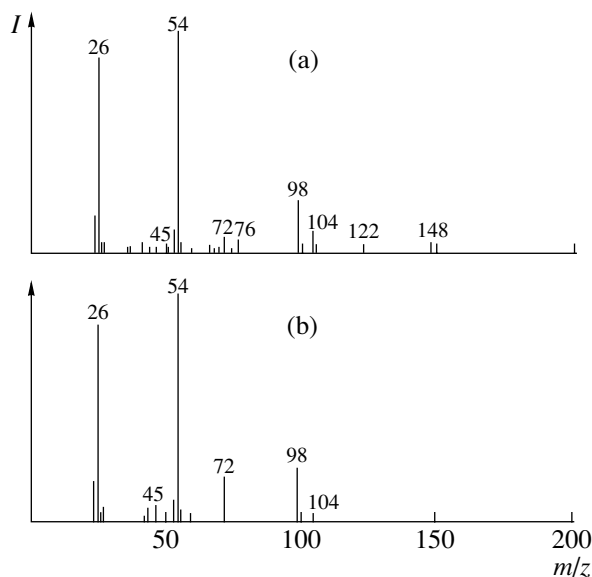

Fig. 7. Mass spectra of the oxidation products of (a) 1-C_4H_8 and (b) n-C_4H_{10}.

To test the third hypothesis, we used the well-known high activity of VPO catalysts in the alcohol dehydration reaction [37]. We studied the oxidation of 1-butanol in the presence of the VPO catalyst. Figure 8 shows the temperature dependence of product concentrations in this reaction. As can be seen, at sufficiently low temperatures (140°C), alcohol dehydration came into play with the formation of butene-1, the only par-
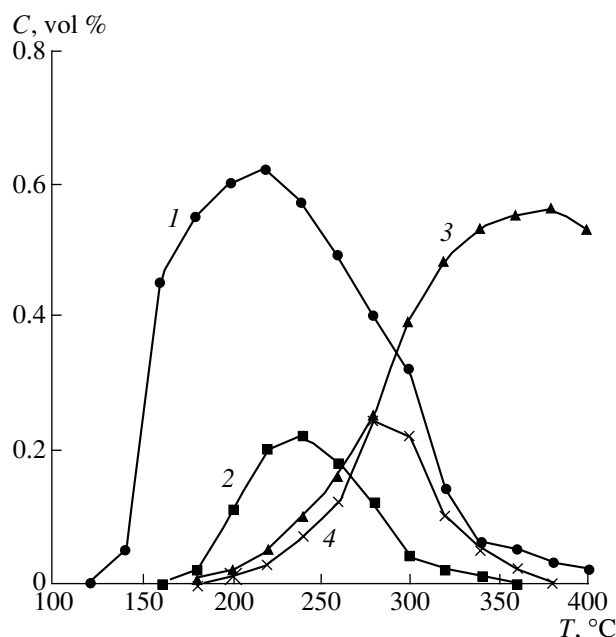
Fig. 8. The temperature dependence of product formation in the oxidation of 1-C_4H_9OH: (*1*) C_4H_8, (*2*) C_4H_6, (*3*) $C_4H_2O_3$, and (*4*) $C_8H_4O_3$.

tial oxidation product. An increase in the temperature led to the appearance of butadiene-1,3 in the reaction products and then to the formation of maleic anhydride. As the reaction temperature was further increased, phthalic anhydride was detected in the products. To 280°C, its concentration increased (selectivity to phthalic anhydride was 30 mol %); thereafter, it began to decrease. With the appearance of phthalic anhydride, the concentrations of butene and butadiene began to decrease. At temperatures higher than 360°C, only maleic anhydride and butene-1 traces were present in the reaction products of partial oxidation. In this case, the selectivity to maleic anhydride was higher than 50 mol %, which is consistent with previously published data [23, 38]. Consequently, the experimental results provide support for a difference in the properties of C_4 unsaturated structures formed in the course of catalytic reaction on the catalyst surface and olefins adsorbed from a gas phase.

Thus, the experimental results support the reaction scheme proposed for product formation in the partial oxidation reaction of *n*-pentane with the primary elimination of a methyl group, which leads to the formation of C_4 unsaturated hydrocarbon surface structures. Next, these structures are oxidized to maleic anhydride. The Diels–Alder reaction between maleic anhydride and C_4 unsaturated structures leads to the formation of phthalic anhydride, and the low steady-state concentration of these structures limits this process.

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