ELSEVIER Catalysis Today 32 (1996) 243–253

CATALYSIS TODAY

The reaction network of the selective oxidation of n-butane on $(VO)_2P_2O_7$ catalysts: Nature of oxygen containing intermediates

B. Kubias [a,*], U. Rodemerck [a], H.-W. Zanthoff [b], M. Meisel [c]

[a] *Institut für Angewandte Chemie Berlin-Adlershof, Rudower Chaussee 5, D-12484 Berlin, Germany*
[b] *Lehrstuhl für Technische Chemie, Ruhr-Universität Bochum, D-44780 Bochum, Germany*
[c] *Institut für Chemie, Humboldt Universität zu Berlin, Hessische Str. 1-2, D-10115 Berlin, Germany*

Abstract

The reaction network of the partial oxidation of n-butane to maleic anhydride on $(VO)_2P_2O_7$ has been investigated using steady-state and transient experiments in a Temporal-Analysis-of-Products (TAP) reactor under vacuum conditions to identify by mass spectrometry possible intermediate products and in a tubular fixed bed reactor at atmospheric pressure to derive information on the role of the detected and other potential intermediates in the reaction network. The oxidation of butane, butadiene, tetrahydrofuran, dihydrofuran, and furan has been studied in the TAP reactor and, additionally to these compounds, crotonaldehyde, crotonlactone, and malealdehydic acid were oxidized in the tubular flow reactor. From the results obtained it can be concluded that the main reaction pathway from butane to maleic anhydride proceeds via the intermediate products n-butenes, butadiene, crotonaldehyde, dihydrofuran, furan, and crotonlactone.

Keywords: n-Butane oxidation; Maleic anhydride; VPO catalyst; Reaction mechanism

---

1. Introduction

The conversion of n-butane to maleic anhydride (MA) is a complex selective oxidation reaction which includes the abstraction of 8 hydrogen atoms and the insertion of 3 oxygen atoms into the C_4 molecule. Although it is obvious that this reaction requires several reaction steps, no intermediates have been observed up to now during the oxidation of hydrocarbon lean butane–air mixtures on selective and active equilibrated catalysts under steady-state conditions and atmospheric pressure [1]. This finding caused some authors to postulate reaction mechanisms in which the butane molecule is activated in the C_1 and C_4 position [2,3] and, after cleavage of the respective C–H bonds, it is anchored on the catalyst surface via one or two oxygen bridges [2–5]. Thereafter, the reaction runs without desorption of any intermediates to MA which then finally desorbs. Only on $(VO)_2P_2O_7$ promoted with a lanthanum additive the detection of tetrahydrofuran originated from such an intermediate structure was claimed [2]. In contrast to these ideas on the reaction mechanism, Pepera et al. [6] have shown by oxidation of partly deuterated butane that butane activation occurs mainly at the C_2 and C_3 methylene groups and, indeed, products of oxidative

---

[*] Corresponding author.

PII S0920-5861(96)00167-8

dehydrogenation of the butane molecule, the butenes and butadiene resulting from such an intermediate structure, could be determined under particular reaction conditions [7,8]. Additionally, furan was identified as another possible intermediate among the reaction products under oxygen-deficient conditions at ambient pressure [7], and at vacuum conditions in transient experiments using the Temporal-Analysis-of-Products (TAP) reactor [8].

Basing on these results, a reaction chain from butane via butenes, butadiene and furan to MA seems to be the most likely one. But some questions remain unanswered, e.g., if tetrahydrofuran is really an intermediate product and via which intermediates the reaction steps from butadiene to furan and from furan to MA proceed. 2,5-dihydrofuran and crotonlactone (2-butene-1,4-olid), respectively, have been discussed to be intermediates in these steps [1,9]. Up to now, only crotonaldehyde, a potential intermediate in the step from butadiene to furan, could be identified in a desorption experiment as a product of the oxidation of butane on $(VO)_2P_2O_7$ catalysts [10]. Special TAP experiments were carried out to detect dihydrofuran using a pretreated catalyst but they were not successful [9]. In the oxidation of butadiene, however, the intermediate products mentioned above were detected on a supported vanadium oxide catalyst with short pores and low density of the oxidizing sites [11]. Malealdehydic acid (β-formylacrylic acid, 5-hydroxy-2-oxo-2,5-dihydrofuran) is known to be an oxidation product of the liquid phase oxidation of furan and furfurol, respectively, with triplet or singlet dioxygen [12]. In principle, the formation of this product via insertion of oxygen from the catalyst into a furan molecule could be possible and, therefore, malealdehydic acid should be taken into account for the step furan to MA in addition to crotonlactone.

It was the aim of the present work to elucidate oxygen insertion steps into the C_4 molecule by identification of possible intermediates studying the C_4 oxidation at steady-state and transient conditions in vacuum with the TAP reactor. Additionally, some possible intermediates were oxidized in a tubular catalytic fixed bed reactor at atmospheric pressure to derive information on their role in the reaction network. Further, it was of interest to study if phthalic anhydride is formed in the oxidation of butane, analogously to its formation in the oxidation of pentane [13].

Concerning other topics of butane oxidation, e.g., the type of mechanism operating in the different steps of the butane oxidation to MA (redox mechanism or not) and the role of the different valence states of vanadium (V^{4+} or V^{5+}) in the mechanism we refer to our previous studies [14,15].

2. Experimental

2.1. Catalysts

The $(VO)_2P_2O_7$ catalysts used in this work were obtained from a sulfate containing precursor $VOHPO_4 \cdot 0.5H_2O$ and a precursor $VOHPO_4 \cdot 4H_2O$. Both were prepared from aqueous solution and, therefore, did not contain any intercalated alcohol. For further details of the synthesis of the precursors and their physico-chemical properties see Ref. [16].

The conditioned catalyst specimen used in the TAP studies was obtained by a short time pretreatment of the fresh, ''calcined'' $(VO)_2P_2O_7$ catalyst with a butane–air mixture at a temperature at which the butane conversion was nearly complete. Its average oxidation state of vanadium was 4.022. The principle of the pretreatment procedure of that fresh $(VO)_2P_2O_7$ catalyst which was prepared by calcining the precursor in a stream of nitrogen at 480°C is described in [16] (''high-temperature short-time pretreatment'').

The catalyst for the flow reactor study was prepared as a well crystallized $(VO)_2P_2O_7$ by calcining the $VOHPO_4 \cdot 4H_2O$ precursor in a stream of nitrogen at 650°C and was used without any pretreatment procedure. Its average valence state of vanadium amounted to 4.0.

2.2. Feeds

The following substrates were used in experiments for oxidation and identification of intermediate and side products:

n-butane, butadiene, tetrahydrofuran, dihydrofuran, furan, crotonlactone, and $^{18}O_2$, all were of more than 99% purity. Crotonaldehyde was freshly distilled prior to the oxidation study. Malealdehydic acid was synthesized according to Schenck by photosensitized oxygenation of furfurol [12].

The reactant mixtures for the TAP experiments (organic substrates: n-butane, butadiene, dihydrofuran and furan) were prepared in a feed mixing vessel of the TAP apparatus. Neon was usually used as internal standard (10%). The C_4 compounds were oxidized under anaerobic conditions or as mixtures with $^{16}O_2$ and with $^{18}O_2$, respectively (O_2:C_4 substrate = 3.3–5.9:1).

The reactant mixtures for the steady-state flow experiments at atmospheric pressure were prepared as follows: Gaseous or volatile substrates were mixed with N_2 and O_2 in suitable steel bottles. Usually the concentration of the substrate was 0.8–1.0 Vol% and the oxygen concentration amounted to 20%. For standardization, the concentration of the organic substances was determined by oxidizing them over a Co_3O_4 catalyst and measuring the amount of CO_2 formed by infrared photometry.

Less volatile compounds like crotonlactone and malealdehydic acid were dosed by saturating a stream of N_2 bubbling through the liquids at given temperatures. After mixing the substrate-containing N_2 stream with O_2 the partial pressures of the substrates were estimated via total oxidation as already mentioned. Malealdehydic acid is able to isomerize to fumaraldehydic acid at elevated temperatures. Therefore, its actual partial pressure was controlled using a combination of total oxidation and IR photometry as mentioned above.

2.3. Reactors and experimental procedures

The TAP reactor system has been described in detail by Gleaves et al. [17]. The principle of the method and the conditions being of interest for the present study are reported in [14]. Therefore, only a short remark on the TAP procedure is presented here.

In the TAP study two different modes of operation were used. At "scan mode" pure substrates or substrate-oxygen mixtures were passed as a continuous flow over the catalyst and scanned mass spectra were recorded. At "pulse mode" small amounts of approx. 10^{16} molecules of gas mixtures were pulsed to the catalyst and the response signals to a single m/e at the reactor outlet were recorded with time. The reaction temperatures amounted to 420°C or 445°C (scan mode experiments) and 420°C (pulse mode).

For the steady-state experiments a conventional tubular fixed bed reactor was used which was made of stainless steel. The charge of catalyst having granuled shape (1,25–2,5 mm) amounted to 10–30 ml. The reaction products were analyzed and identified by off-line and on-line GC using packed columns of different polarity (see also [18]).

3. Results

3.1. Steady-state and transient studies under vacuum conditions

3.1.1. Anaerobic oxidation of butane: Reaction intermediates and side products

n-butane was passed over the conditioned catalyst specimen in the absence of gaseous oxygen at 445°C to determine reaction intermediates and products. Fig. 1 shows a typical scanned mass spectrum of the reaction products. From this spectrum the presence of n-butane (m/e = 58) and the formation of butene (m/e = 56), butadiene (m/e = 54), furan (m/e =

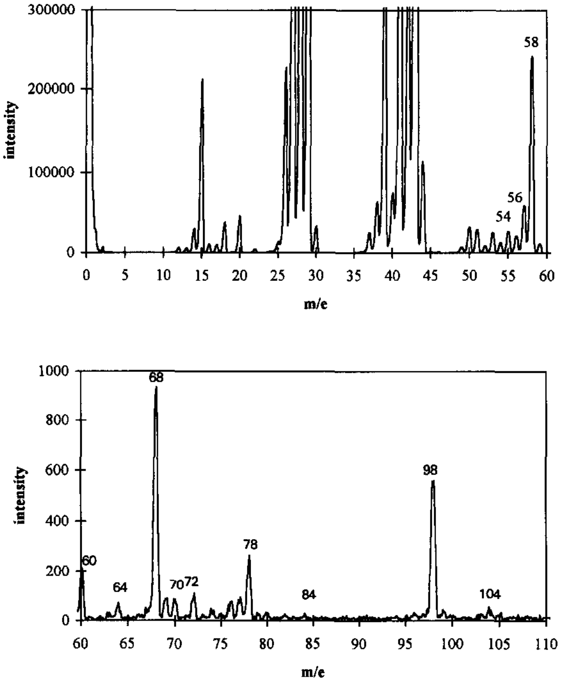


Fig. 1. Scanned mass spectrum of the products of an continuous flow anaerob butane oxidation experiment on a conditioned $(VO)_2P_2O_7$ catalyst at 445°C.

68), and MA (m/e = 98) can be concluded. In case of m/e = 54 and 56 corrections of the intensities measured were necessary because these fragments are also present in the mass spectra of other products [14]. Further, the total oxidation product CO_2 is identifiable (m/e = 44) whereas the estimation of CO is difficult due to the formation of fragments with m/e = 28 from most of the other reaction products. Molecular ions and typical fragments of reaction products are summarized in Table 1.

The small peak at m/e = 70 might be attributed to both the molecular ion of crotonaldehyde and the molecular ion of dihydrofuran. A comparison of the mass spectra of the respective pure compounds reveals that they are very similar. Only the fragments at m/e = 27 and 42 could be used for discrimination but at these m/e fragments of other reaction products appear, too. A small peak at m/e = 72 was also found which could be the molecular peak of tetrahydrofuran. A comparison with the mass spectrum of tetrahydrofuran shows that in the mass spectrum of this compound at m/e = 71 a second peak of similar intensity occurs which, however, was not observed. Considering the fact that acrylic acid (molecular ion: m/e = 72) is a well known side product of the selective butane oxidation under steady-state conditions it

Table 1
Molecular ions and fragments used for the identification of reaction products of the aerobic and anaerobic oxidation of butane, butadiene, dihydrofuran and furan

Molecule	Used molecular ions and fragments (m/e) in case of	
	oxygen free or ^{16}O containing molecules	^{18}O containing molecules
n-Butane	54, 56, 58	
Butenes	54, 56	
Butadiene	54	
Tetrahydrofuran	71, 72	73, 74
2,5- and 2,3-Dihydrofuran	70	72
Crotonaldehyde	70	72
Furan	68	70
Crotonlactone	84	86, 88
Malealdehydic acid	100	102, 104, 106
MA	98	100, 102, 104
CO_2	44	46, 48
Acrylic acid	72	74, 76
Acetic acid	60	62, 64
Phthalic anhydride	104	106

Table 2
Oxidation of butane, butadiene, 2,5-dihydrofuran and furan over a conditioned $(VO)_2P_2O_7$ catalyst

Substrate	Oxygen	Mass spectrometric analysis, detected m/e													
	68	70	71	72	74	76	84	86	88	98	100	102	104	106	
Butane	–	+	+		+	+		tr.			+			tr.	
Dihydrofuran	–	+	+	+	+	+	+	+			+		+	+	+
Butane	$^{16}O_2$	+	tr.								+				
Butadiene	$^{16}O_2$	+	tr.		+	tr.	n.m.	tr.			+			+	
Butane	$^{18}O_2$	+	+	tr.	+	+	+	tr.	tr.	tr.	+	+	+	+	+
Butadiene	$^{18}O_2$	+	+	tr.	+	+	+	+	+	+	+	+	+	+	+
Furan	$^{18}O_2$	+	+	tr.	+	+	+	+	+	tr.	+	+	+	+	n.m.

+ peak detected, tr. traces, n.m. not measured in this m/e region.

is probable that the observed peak originates from this compound.

The small peak at m/e = 84 could be the molecular ion of a compound with the formula $C_4H_4O_2$. No peak at m/e = 100 which could be attributed to the molecular ion of malealdehydic acid was observed at the reaction conditions chosen. The m/e = 104 might be the fragment $C_7H_4O^+$ originated from the phthalic anhydride molecule by loss of CO_2 [19].

3.1.2. Aerobic oxidation experiments

In order to identify the m/e = 84 and 104 as well as other interesting masses (m/e = 60, 64, 78) which can be related to mechanistic aspects but could not be assigned to experiments were carried out at 445°C using n-butane, butadiene, dihydrofuran, furan, $^{16}O_2$ and $^{18}O_2$, respectively, as reactants. The results of these experiments are summarized in Table 2.

When passing a continuous flow of a mixture of $^{16}O_2$ and butane at 420°C over the conditioned catalyst, a small peak at m/e = 84 appeared and a bigger one at this m/e ratio was found in the oxidation of butadiene, dihydrofuran or furan under the same conditions. Oxidation with $^{18}O_2$ resulted in two additional peaks with m/e = 86 and 88 in the scanned mass spectra of the products of the oxidation of butane, butadiene and furan as shown in Fig. 2. Based on this finding it is strongly suggested that a product with two oxygen atoms is formed which could be crotonlactone or butenedial. The occurrence of the three different m/e men-

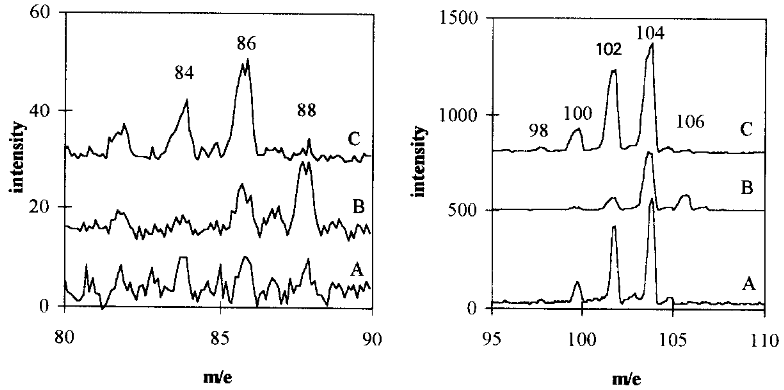


Fig. 2. Mass spectra m/e = 80–90 and m/e = 95–110 of the oxidation products of C_4 oxidation with $^{18}O_2$ on a conditioned $(VO)_2P_2O_7$ catalyst, T = 420°C, feeds: butane/$^{18}O_2$ (A), butadiene/$^{18}O_2$ (B), and furan/$^{18}O_2$ (C). The spectra of the oxidation products of butadiene and furan were shifted to higher intensities.

tioned above is analogous to the formation of MA molecules with the molecular ions m/e = 98, 100, 102 and 104 in which different amounts of ^{18}O are inserted. Both possible intermediates, crotonlactone and butenedial, show similar mass spectra [19,22] and, therefore, cannot be discriminated under the conditions applied. In all these experiments with mixtures containing $^{16}O_2$ no molecular ion of malealdehydic acid at m/e = 100 was observed in accordance with the finding in the anaerobic oxidation of butane.

Concerning the m/e = 104, the oxidation of butadiene, dihydrofuran and furan resulted in distinct peaks at this m/e whereas in the butane oxidation only traces of this fragment were found. The mass spectra of oxidation products obtained with $^{18}O_2$ as oxidant exhibited the additional formation of the m/e = 106 corresponding to a fragment in which the ^{16}O is substituted by ^{18}O (Fig. 2). Therefore, this fragment should be $C_7H_4O^+$ mentioned above as a derivative of phthalic anhydride.

Oxidation of butane with $^{18}O_2$ resulted in the appearance of a peak at m/e = 62 additionally to m/e = 60 and in the increase of m/e = 64. This finding probably originates from a fragment or molecular ion containing two oxygen atoms. Thus, it can be assigned to acetic acid. Analogously, the formation of additional peaks at m/e = 74 and 76 supported the conclusion that the peak at m/e = 72 may be attributed to acrylic acid. The peak at m/e = 64 is caused by the loss of SO_2 from the SO_4^{2-} containing $(VO)_2P_2O_7$ catalyst specimen as was confirmed by the mass spectrum of the gaseous products obtained by heating the catalyst in vacuum. The peak at m/e = 78 should belong to a product without any oxygen content because of the lack of the masses 80 or 82 in case of the experiments with $^{18}O_2$.

3.1.3. Single pulse experiments

TAP response signals were recorded for the m/e = 54, 56, 58, 68 and 98 in the anaerobic oxidation of butane. The recording of the m/e = 84 was given up due to the very small intensity of this peak. In accordance with the results described by Ebner et al. [8] the elution times of the peak maxima of the different molecular ions were in the sequence butane, butene, butadiene, furan and MA. Additionally, the shapes of the response curves were also similar.

3.2. Steady-state experiments at ambient pressure: Oxidation of intermediates in the flow reactor

To evaluate the role of possible intermediates, tetrahydrofuran, dihydrofuran, crotonaldehyde, crotonlactone, and malealdehydic acid were oxidized at conditions of excess of oxygen. Additionally, n-butane and the intermedi-

Table 3
Oxidation of butane and of possible intermediates to MA over a $(VO)_2P_2O_7$ catalyst with an average vanadium valence state of 4.0

Substrates [d]	$Y_{MA\ max}$ [Mol%]	$T_{90\%}$ [°C]	$\tau_{90\%}$ [s]	Compounds observed	$Y_{I\ max}$ [Mol%]
Butane	43	460	1.60	–	–
Tetrahydrofuran	49	355	1.50	n.e. [a]	n.e.
Butadiene	48	430	0.36	F [b]	8
				CA [c]	0.7
2,5-Dihydrofuran	51	350	0.40	F	79
Crotonaldehyde	50	380	0.36	F	19
Furan	65	375	0.36	–	–
Crotonlactone	54	370	0.39	–	–
Malealdehydic acid	68	372	0.40	–	–

[a] Not estimated, [b] F = furan, [c] CA = crotonaldehyde, [d] 0.8–1.0 vol% in air.
$Y_{MA\ max}$, $Y_{I,max}$: Maximum yield of MA and intermediate product, respectively.
$\tau_{90\%}$: Residence time at 90% conversion at $T_{90\%}$.
$T_{90\%}$: Temperature of 90% conversion of the substrate at $\tau_{90\%}$.

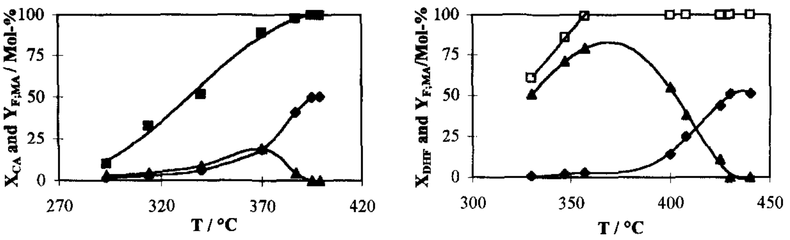


Fig. 3. Oxidation of crotonaldehyde and 2,5-dihydrofuran on $(VO)_2P_2O_7$: Conversion of the substrates and formation of MA and furan in dependence on temperature. Catalyst: $(VO)_2P_2O_7$. Concentration of substrates: 1% in air, $\tau_{90\%}$: s. Table 2. ■ $X_{\text{Crotonaldehyde}}$, □ $X_{\text{Dihydrofuran}}$, ◆ Y_{MA}, ▲ Y_{Furan}.

ates butadiene and furan were converted to MA to get a basis to compare reactivities and selectivities.

The maximum MA yields, the temperatures of 90% conversion of the substrates under comparable residence times and the yields of possible intermediates are listed in Table 3. The data in this table reveal that both the MA yields and the reactivities of the compounds differ remarkably and, therefore, these results may give hints for the evaluation of the different reaction chains which seem to be possible. Thus, the role of the different intermediates in the reaction steps is assessed as follows: The MA yield obtained in the oxidation of an intermediate product should be equal or higher than the MA yield from that product which is thought to be the "precursor" of the intermediate in the reaction chain. Further, the temperature of 90% conversion of the intermediate mentioned should be lower than that one of the preceding precursor. These criteria are met by the intermediate products tetrahydrofuran, butadiene, crotonaldehyde, dihydrofuran, furan and malealdehydic acid. Crotonlactone does not seem to fulfil these requirements for an intermediate of the step from furan to MA but the change in the reaction system caused by changing a substrate should also be taken into account as it is discussed below.

For illustration, the conversion of dihydrofuran, crotonaldehyde, crotonlactone and malealdehydic acid and the yields of MA and, in case of the two former substrates, of furan, are depicted as a function of temperature in Fig. 3 and Fig. 4. As shown in Fig. 3, with increasing degree of conversion of crotonaldehyde and dihydrofuran the yields of furan run through maxima pointing to the role of furan as an intermediate product as it was found by other authors in case of dihydrofuran oxidation, too [23]. Furthermore, Fig. 3 illustrates that the conversion of dihydrofuran is nearly complete

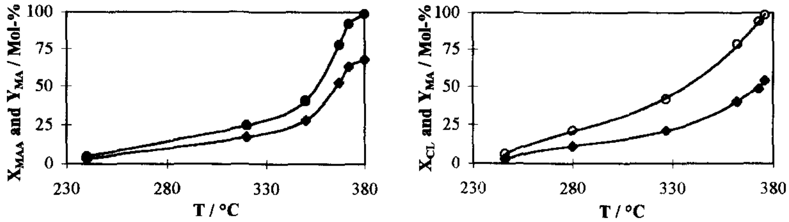


Fig. 4. Oxidation of crotonlactone and malealdehydic acid on $(VO)_2P_2O_7$: Conversion of the substrates and formation of MA in dependence on temperature. Catalyst: $(VO)_2P_2O_7$. Concentration of malealdehydic acid: 0.8–1.0% in air. Concentration of crotonlactone: 1% in air, $\tau_{90\%}$: s. Table 2. ● $X_{\text{Malealdehydic acid}}$, ○ $X_{\text{Crotonlactone}}$, ◆ Y_{MA}.

at the comparatively low temperature of 350°C under the reaction conditions chosen.

4. Discussion

4.1. The reaction steps from butane to MA: Nature of the oxygen containing intermediates

It is concluded from the detection of the m/e = 54, 56 and 68 in the scan mode TAP study and from the sequence of the elution times of the peak maxima at these m/e observed in the single pulse study that the reaction chain butane → butene → butadiene → furan → MA is the most probable one. In contrast, tetrahydrofuran could not be detected by mass spectrometry. Therefore, a reaction path from butane to MA via tetrahydrofuran should be unlikely. This assumption is supported by the results of the flow reactor study: Tetrahydrofuran should have been found in the scanned mass spectrum of the butane oxidation because of its lower reactivity compared with all other intermediates (Table 3). Hence, tetrahydrofuran is ruled out from the reaction mechanism considering the fact that the experimental proofs of the existence of this intermediate presented in Ref. [2] are described in such a way that a real evaluation of these results is difficult.

4.2. Intermediates in the reaction step butadiene → furan

From the results of the flow reactor experiments listed in Table 3 it follows that both dihydrofuran and crotonaldehyde could play a role as intermediate products in the reaction step from butadiene to furan. Therefore, it is discussed whether one or both of these compounds are intermediates in this reaction step. This question cannot be answered by the steady-state vacuum method applied: The mass spectra of dihydrofuran and crotonaldehyde differ so little that it is impossible to distinguish between these products. Therefore, transient experiments for the identification of dihydrofuran or crotonaldehyde analogous to those carried out by Centi et al. [9] were given up from the start.

Only crotonaldehyde was found among the reaction products of the butane oxidation in a stopped flow desorption experiment at a temperature about 100°C higher than steady-state butane oxidation temperatures [20]. This finding was interpreted by the authors assuming a possible role of crotonaldehyde as a precursor of the formation of total oxidation products. Our experimental results, i.e., the high MA yield which can be obtained from crotonaldehyde and its high reactivity contradict this interpretation. From the detection of crotonaldehyde mentioned and from the fact that dihydrofuran was not identified as a product of the oxidation of butane up to now, it might be concluded that crotonaldehyde is the only intermediate. However, the fact that dihydrofuran was not detected can be explained by the very high reactivity of this compound: As it is demonstrated in Fig. 3 and from the result of a respective transient experiment, too, 2,5-dihydrofuran is converted into furan at very low temperatures. Furthermore, this compound was found among the reaction products of the oxidation of butadiene on the supported vanadium oxide catalyst with special pore structure mentioned above beside considerable amounts of crotonaldehyde [11]. This finding supports the assumption that the reaction path from butadiene to furan proceeds via dihydrofuran also on $(VO)_2P_2O_7$ catalysts. The formation of 2,5-dihydrofuran can be assumed to occur via enolization of crotonaldehyde followed by intramolecular cyclization of the intermediate 1,3-butadiene-1-ol with subsequent isomerization of the formed 2,3-dihydrofuran. The consecutive oxidative dehydrogenation step to furan proceeds so fast that dihydrofuran cannot be detected under usual reaction conditions. Analogous results were reported by Centi et al. [23], too. Because of this very rapid formation of furan, reaction pathways from dihydrofuran to other intermediates, e.g. crotonlactone, as suggested in [20] should rather play a minor role in the reaction network but they cannot be excluded on the basis of the results described.

4.3. Intermediates in the reaction step furan → MA

The TAP reactor experiments with mixtures containing $^{18}O_2$ and different organic substrates exhibited the formation of a reaction product, being characterized by peaks at $m/e = 84$, 86 and 88 which contains two oxygen atoms and which is formed also in the oxidation of furan. The latter fact leads to the suggestion that this product is crotonlactone because its formation from furan should be more likely than the formation of butenedial by opening the heterocyclic furan ring. The assumption that crotonlactone is the missing link in the step from furan to MA is also confirmed by the detection of this intermediate in the butadiene oxidation on a supported vanadium oxide catalyst [11] and by an IR spectroscopic investigation which revealed the existence of a crotonlactone-derived adsorbate structure in the oxidation of furan to MA on a supported VPO catalyst [21]. From our experiments at atmospheric pressure especially the comparable reactivity of crotonlactone and malealdehydic acid is significant. This is evident by the same degree of conversion under similar conditions (Table 3). Thus, malealdehydic acid should have been detected in the transient experiments performed, because of its stronger acidity allowing it to desorb easier than crotonlactone. Therefore, a reaction path from furan to MA via crotonlactone seems to be the more likely one. Discussing the finding that the oxidation of crotonlactone did not result in a higher MA yield in comparison to the oxidation of furan (Table 3) it should be considered that the kinetics of the oxidation of crotonlactone and of furan should not be necessarily the same and, therefore, the oxidation state of the catalyst surface can be different. This could result in different selectivity properties taking into account the remarkable influence of the oxygen availability of the $(VO)_2P_2O_7$ surface on MA selectivity as shown by Schuurman et al. in a TAP reactor study on butane oxidation [24]. Therefore, the additional experimental hints given above referring to the role of crotonlactone as intermediate product should be considered to a larger extent.

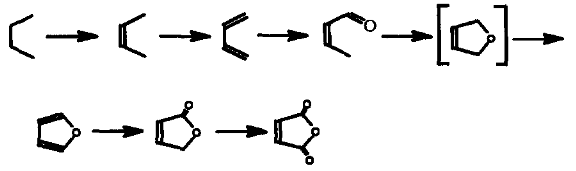
4.4. Side products in the oxidation of n-butane

The results of the transient studies presented above show that phthalic anhydride is a side product of the butane oxidation. It could be formed analogously as in the oxidation of n-pentane as discussed by Centi et al. [13]. According to these authors, after oxidative dehydrogenation of pentane to cyclopentadiene, the dimerization of two cyclopentadiene molecules takes place followed by further oxidation and degradation of the dimer to phthalic anhydride. In case of butane oxidation Diels-Alder additions between the diene components butadiene and furan and the monoene components MA, crotonlactone, crotonaldehyde and dihydrofuran seem to be possible. In the reactions of butadiene with one of the activated olefinic compounds consecutive oxidative dehydrogenation steps of the addition products formed must be involved in order to form phthalic anhydride. In contrast, after a reaction of furan with one of the monoenes, an intramolecular dehydration step of the intermediate endooxide seems to be necessary in the reaction chain to phthalic anhydride.

The other side products, acrylic acid and acetic acid, might be formed by oxidation of the intermediates butadiene, but-2-ene and furan, respectively, with cleavage of the C–C double bond. The peak at $m/e = 78$ found in the oxidation of butane, butadiene and furan, is assigned to benzene, a product which was also found in the butadiene oxidation on the vanadium oxide catalyst mentioned above [11].

5. Conclusions

From the results presented it is concluded that the oxidation of butane to MA proceeds according to the following scheme:



Crotonaldehyde, dihydrofuran and crotonlactone are assumed to be intermediate products in the main reaction path, additionally to the well known butene, butadiene and furan intermediates. The reaction chain suggested is based on the identification of compounds which could be intermediate products for structural reasons and because of their reactivity and selectivity properties derived from catalytic oxidation experiments of these potential intermediates under steady-state conditions. Therefore, the non detected intermediate dihydrofuran is put in brackets despite the fact that its formation is very probable. However, parallel reaction routes certainly cannot be ruled out, e.g., a route from crotonaldehyde via butenedial to MA, but such a pathway was not supported by a doubtless detection of the respective intermediate product.

Further research is necessary to find out additional proofs for the mechanism proposed above. However, doing this it must be taken into account that in oxidation experiments utilizing intermediate products under steady-state conditions the problem must be overcome that in the oxidation of each intermediate the kinetics is different from that in the steady-state of the butane oxidation. Therefore, such experiments do not certainly allow to conclude whether the respective intermediate is situated on the main reaction path or on a parallel pathway of minor importance. Transient experiments at ambient pressure including the change from the steady-state of butane oxidation to the steady-state of oxidation of an intermediate should help to answer these questions.

Acknowledgements

The financial support of this work by the Deutsche Forschungsgemeinschaft (DFG) and the Bundesministerium für Bildung, Wissenschaft, Forschung und Technologie (BMBF) is gratefully acknowledged by the authors.

References

[1] F. Cavani and F. Trifirò, Catalysis, 11 (1994) 247.
[2] V.A. Zazhigalov, J. Haber, J. Stoch, G.A. Komashko, A.I. Pyatnitskaya and I.V. Bacherikova, Stud. Surf. Sci. Catal., 82 (1994) 265.
[3] J. Ziolkowski, E. Bordes and P. Courtine, J. Catal., 122 (1990) 126.
[4] Y. Zhang-Lin, M. Forissier, R.P. Sneeden, J.C. Védrine and J.C. Volta, J. Catal., 145 (1994) 256.
[5] Y. Zhang-Lin, M. Forissier, J.C. Védrine and J.C. Volta, J. Catal., 145 (1994) 267.
[6] M.A. Pepera, J.L. Callahan, M.J. Desmond, E.C. Milberger and P.R. Blum, N.J. Bremer, J. Am. Chem. Soc., 107 (1985) 4883.
[7] G. Centi, G. Fornasari and F. Trifirò, J. Catal., 89 (1984) 44.
[8] J.R. Ebner, J.T. Gleaves, in A.E. Martell and D.T. Sawyer, Eds., Oxygen Complexes and Oxygen Activation by Transition Metals, Plenum Publishing Corp., 1988, p. 273.
[9] G. Centi, F. Trifirò, J.R. Ebner and V.M. Franchetti, Chem. Rev., 88 (1988) 73.
[10] G. Busca, G. Centi and F. Trifirò, in B. Delmon and G.F. Froment, Eds., Catalyst Deactivation, Elsevier Science B.V., Amsterdam, 1987, p. 427.
[11] D. Hönicke, J. Catal., 105 (1987) 10.
[12] G.O. Schenck, Liebigs Ann. Chem., 584 (1953) 156.
[13] G. Centi, J.T. Gleaves, G. Gollinelli and F. Trifirò, Stud. Surf. Sci. Catal., 72 (1992) 281.
[14] U. Rodemerck, B. Kubias, H.W. Zanthoff and M. Baerns, Appl. Catal., in press.
[15] U. Rodemerck, B. Kubias, H.W. Zanthoff, G.-U. Wolf and M. Baerns, Appl. Catal., in press.
[16] B. Kubias, M. Meisel, G.-U. Wolf and U. Rodemerck, Stud. Surf. Sci. Catal., 82 (1994) 195.
[17] J.T. Gleaves, J.R. Ebner and T.C. Kuechler, Catal. Rev.-Sci. Eng., 30 (1988) 49.
[18] B. Kubias, H. Wolf and B. Jacobi, Chem. Techn., 46 (1994) 63.
[19] E. Stenhagen, S. Abrahamsson and F.W. McLafferty, Eds.,

Registry of Mass Spectral Data, Vols. 1–4, Wiley, New York, 1974.

[20] G. Centi, F. Trifirò, G. Busca, J.R. Ebner and J.T. Gleaves, Proc. 9th Int. Congr. on Catalysis, 4 (1988) 1538.

[21] A. Ramstetter and M. Baerns, J. Catal., 109 (1988) 303.

[22] P.B. Shepson, E.O. Edney and E.W. Corse, J. Phys. Chem., 88 (1984) 4122.

[23] G. Centi and F. Trifirò, J. Mol. Catal., 35 (1986) 255.

[24] Y. Schuurman and J.T. Gleaves, Ind. Eng. Chem. Res., 33 (1994) 2935.