

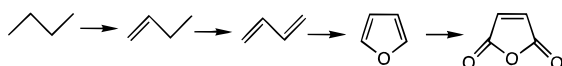
## Evidence for Two Competing Mechanisms for *n*-Butane Oxidation Catalyzed by Vanadium Phosphates

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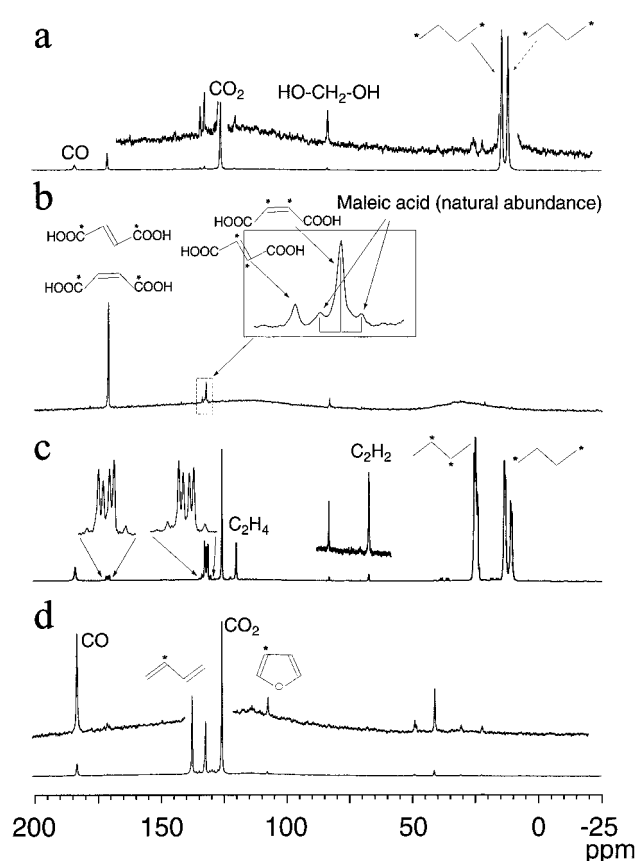
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The conversion of *n*-butane to maleic anhydride by vanadium phosphorus oxide (VPO) catalysts is recognized as one of the most complex selective oxidation reactions used in industry today, as it involves the abstraction of eight hydrogen atoms and insertion of three oxygen atoms.<sup>1–3</sup> The reaction is proposed to proceed by either an alkoxide or an olefinic intermediate route. Under standard operating conditions no intermediates have been observed in the reaction products, so the proposed mechanisms for this reaction are based upon studies of the kinetics of the reaction and the observation of anticipated intermediates using nonstandard conditions.<sup>3,4</sup> In the olefinic route, the reaction is proposed to proceed as shown:



This route is based on the observation of butenes, butadiene, and furan at very low concentrations (<2%) in the reaction products using low oxygen and high *n*-butane concentrations on catalysts with average vanadium oxidation states  $\sim 4$  or below.<sup>2,5,6</sup> For this reason the role of the proposed intermediates in the reaction mechanism has been questioned.<sup>2,3</sup> However, all of the intermediates react on VPO to produce maleic anhydride significantly faster than does *n*-butane. This has been used to explain why it is difficult to observe these intermediates in the reaction products. In this paper we present the first direct evidence from isotopic labeling studies that the mechanism for *n*-butane oxidation proceeds via two different routes.

We have investigated the conversion of *n*-butane to maleic anhydride by reacting selectively <sup>13</sup>C-labeled *n*-butane on VPO catalysts.<sup>7</sup> The products were collected, sealed in a glass ampule, and analyzed using <sup>13</sup>C NMR spectroscopy.<sup>8</sup> Figure 1a shows the <sup>13</sup>C NMR spectrum of the reaction products collected after flowing 1,4-<sup>13</sup>C-labeled *n*-butane over VPO catalyst at 380 °C that has an average vanadium oxidation state of +4.56 (denoted VPO 4.56). No molecular oxygen was present in this experiment. The



**Figure 1.** <sup>13</sup>C NMR spectra of the reaction products of *n*-butane or butadiene on VPO 4.56. (a) 1,4-<sup>13</sup>C *n*-butane reacting at 380 °C and (b) same as part a, except the ampule was evacuated prior to sealing. Arrows indicate <sup>13</sup>C satellites from 2,3 carbons in 1,4-<sup>13</sup>C maleic acid. (c) Uniformly <sup>13</sup>C-labeled *n*-butane reacting at 380 °C. (d) 2-<sup>13</sup>C butadiene reacting at 330 °C. In all spectra dashed and solid lines indicate gas and liquid peaks, respectively.

spectrum contains large peaks for unreacted gas and liquid phase *n*-butane, as well as CO, CO<sub>2</sub>, ethylene, maleic acid, fumaric acid, and methanediol.<sup>9</sup>

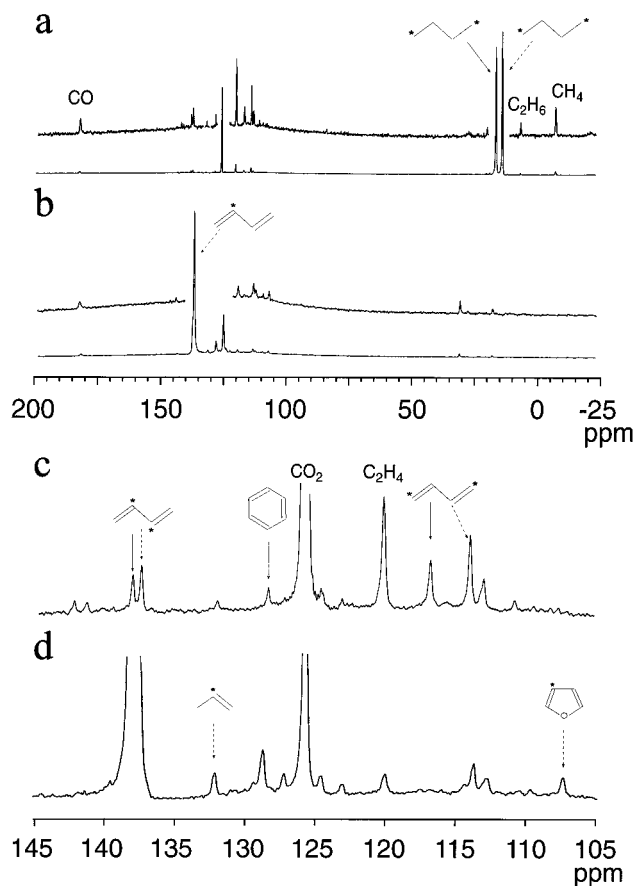
All of the proposed reaction mechanisms indicate that 1,4-<sup>13</sup>C *n*-butane will produce 1,4-<sup>13</sup>C maleic acid (peak at 170 ppm). While most of the maleic acid is labeled in the 1,4 positions, there is a peak corresponding to maleic acid in which the labeled carbons are in the 2,3 positions (132 ppm). The assignment of the 132 ppm peak was confirmed by reacting 1,4-<sup>13</sup>C *n*-butane on VPO 4.56 at 380 °C and evacuating the ampule prior to analysis (Figure 1b). All gaseous and volatile species such as CO, CO<sub>2</sub>, and unreacted *n*-butane were removed, leaving only peaks for maleic acid, fumaric acid, and methanediol in the spectrum.

(8) The VPO catalyst ( $\sim 0.2$  g) was placed in the center of a glass reactor. The reactor was attached to a high-vacuum line and evacuated to less than  $5 \times 10^{-3}$  Torr. The reactants (butane or butadiene,  $\sim 50$   $\mu$ mol) were condensed in one end of the reactor with liquid N<sub>2</sub>. After the catalyst was preheated in a furnace to the desired temperature, liquid N<sub>2</sub> was shifted to the other end of the reactor. After the products were collected, the glass ampule containing the reaction products and the remaining reactant was flame sealed for NMR analysis. <sup>13</sup>C NMR spectra were acquired on a home-built spectrometer operating at 50.197 MHz. Single-pulse <sup>13</sup>C excitation (Bloch decay) with proton decoupling (pulse delay = 1–3 s, 10000–100000 transients) was used to obtain all of the spectra shown.

(9) The assignment of the peaks at 84, 132, and 133 ppm to methanediol, maleic acid, and fumaric acid, respectively, was made by comparison to <sup>13</sup>C chemical shifts and coupling constants in solution and by determining the number of attached protons from the proton coupled spectrum. From this information the peaks for both fumaric and maleic acid could be assigned unambiguously.

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 (7) Three VPO catalysts used in this study were prepared from two different precursors. VPO 3.92 was prepared by mixing a stoichiometric amount of V<sub>2</sub>O<sub>5</sub> and H<sub>3</sub>PO<sub>4</sub> (85%) in ethanol and refluxing for 16 h. The resulting precursor was blue and identified by XRD as VOHPO<sub>4</sub>·0.5H<sub>2</sub>O. The precursor was then calcined in nitrogen at 550 °C for 3 h. The XRD pattern for the resulting catalyst was consistent with (VO)<sub>2</sub>P<sub>2</sub>O<sub>7</sub>. VPO 4.95 was prepared by calcining the precursor at 450 °C for 24 h in air. For VPO 4.56, the procedure described by Cavani et al. (Cavani, F.; Centi, G.; Trifiro, F. *Appl. Catal.* **1984**, *9*, 191–202) was used. The precursor was then calcined at 380 °C for 3 h in air. The average valence state of vanadium in the VPO catalysts was determined using the potentiometric method described by Niwa and Murakami (Niwa, M.; Murakami, Y. *J. Catal.* **1982**, *76*, 9–16). 1,4- and fully <sup>13</sup>C-labeled *n*-butane were obtained from Isotec. 2-<sup>13</sup>C-labeled butadiene was obtained from Cambridge Isotope Laboratories.

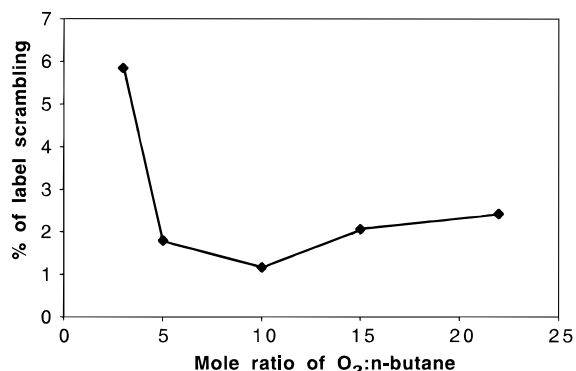


**Figure 2.**  $^{13}\text{C}$  NMR spectra of the reaction products of 1,4- $^{13}\text{C}$  *n*-butane (a) or 2- $^{13}\text{C}$ -butadiene (b) on VPO 3.92 at 540 °C. Parts c and d are expansions of parts a and b, respectively. In all spectra dashed and solid lines indicate gas and liquid peaks, respectively.

The peak assigned to 2,3- $^{13}\text{C}$  maleic acid is bracketed by two smaller peaks assigned to the 2,3 carbons of maleic acid at natural abundance. The resonance of the natural abundance carbons is split into a doublet by  $^{13}\text{C}$ - $^{13}\text{C}$  couplings to the  $^{13}\text{C}$  labels in the 1 and 4 positions of maleic acid. Uniformly  $^{13}\text{C}$  labeled *n*-butane run under identical conditions (Figure 1c) produced essentially the same product distribution, except that the peaks for ethylene and acetylene are much larger than observed for 1,4- $^{13}\text{C}$  *n*-butane. It also shows that the parameters used to acquire the spectrum resulted in the carbonyl resonance of maleic acid being  $\sim 6.5$  times smaller than the olefinic resonance, although the ratio should be 1:1. Spectra acquired with longer repetition times between acquisitions showed that the intensities of all of the other peaks were quantitative. From the integrated intensity ratios of 1:5 for the carbonyl and olefinic resonances, respectively, in Figure 1b and using a scaling factor of 6.5, we estimate that the amount of label exchange for this sample was  $\sim 3\%$ . This is consistent with the intensities of the natural abundance carbons (1.1%) observed in Figure 1b.

We have analyzed over 100 samples of 1,4- $^{13}\text{C}$  *n*-butane reacting on VPO catalysts in average vanadium oxidation states between 4.3 and 5 and at reaction temperatures between 330 and 500 °C and found that the amount of label scrambling varied between 0 and 7%, depending upon both oxidation state and reaction temperature. Label scrambling was greatest at oxidation states  $< 4.6$ , although scrambling was observed at higher oxidation states as well. We explored the possibility that label scrambling occurred when butadiene reacted on VPO. Figure 1d shows the reaction of 2- $^{13}\text{C}$  butadiene on VPO 4.56 at 330 °C. No evidence of label scrambling was observed. This suggests that the label scrambling occurred prior to butadiene formation.

Figure 2a shows the  $^{13}\text{C}$  NMR spectrum of the reaction of 1,4-



**Figure 3.** Effect of the mole ratio of oxygen:*n*-butane on the percentage of label scrambling for *n*-butane and oxygen reacting on VPO 3.92 at 380 °C.

$^{13}\text{C}$  *n*-butane using VPO catalyst with an average vanadium oxidation state of 3.92 (denoted VPO 3.92) under anaerobic conditions at 540 °C. Figure 2c shows the expanded region of Figure 2a. All of the proposed intermediates in the *n*-butane oxidation were observed, and no maleic acid was produced. This result is consistent with previous studies using TAP (temporal analysis of products) reactors and the requirement that  $\text{V}^{5+}$  is necessary for the oxidation to maleic anhydride.<sup>1,5,6,10,11</sup> The most interesting feature is that the peaks for 2,3- $^{13}\text{C}$  butadiene (137–138 ppm) are almost as large as the peaks for 1,4- $^{13}\text{C}$ -labeled butadiene (114–117 ppm). Label scrambling does not occur under identical conditions for 2- $^{13}\text{C}$  butadiene (Figure 2b,d), indicating that it must have occurred prior to the formation of butadiene. The product distribution for reaction temperatures from 450 to 600 °C was identical, indicating that the mechanism for butadiene formation from *n*-butane on VPO 3.92 is independent of reaction temperature.

All of the experiments presented so far were performed using anaerobic conditions. We simulated industrial reaction conditions by running the reaction in the presence of oxygen using VPO 3.92 at 380 °C.<sup>12</sup> The products (CO,  $\text{CO}_2$ , maleic acid, fumaric acid, methanediol, and ethylene) were the same as observed for *n*-butane reacting on VPO 4.56 (Figure 1a). None of the proposed intermediates were observed. The percent of label exchange vs oxygen:*n*-butane ratio is shown in Figure 3. Label scrambling was highest at low oxygen:*n*-butane ratios, decreased until a minimum was reached at about 10:1, and increased slightly at higher oxygen:*n*-butane ratios. This result is consistent with the greatest percentage of label scrambling occurring for low average vanadium oxidation states.

Our results show that the label in butadiene, produced from 1,4- $^{13}\text{C}$  *n*-butane, is completely scrambled, but in maleic acid, also produced from 1,4- $^{13}\text{C}$  *n*-butane, the label is largely unscrambled. This makes it unlikely that maleic acid is formed predominantly by a butadiene intermediate. However, the small amount of label scrambling in maleic acid suggests that both reaction pathways may be occurring simultaneously to produce maleic acid. We are currently investigating the influence of oxidation state and phosphorus-to-vanadium ratios on the percent of label exchange.

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