# In Situ Fourier Transform Infrared Study of Crotyl Alcohol, Maleic Acid, Crotonic Acid, and Maleic Anhydride Oxidation on a V-P-O Industrial Catalyst

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Crotyl alcohol, maleic acid, crotonic (2-butenoic) acid, and maleic anhydride were fed to an in situ infrared cell at 300 °C containing a P/V = 1.1 vanadium-phosphorus-oxide (V-P-O) catalyst used for the selective oxidation of *n*-butane. Crotyl alcohol was used as a mechanistic probe for the formation of reactive olefin species observed during previous n-butane and 1-butene studies. Crotonic acid, maleic acid, and maleic anhydride were fed as probes for the existence of other possible adsorbed intermediates. Olefin species and maleic acid are proposed as possible reaction intermediates in n-butane selective oxidation to maleic anhydride. The involvement of peroxide species in the oxidation of butadiene to maleic acid is also discussed.

### Introduction

Vanadium-phosphorus-oxygen (V-P-O) catalysts are used commercially for the selective oxidation of C4 hydrocarbons to maleic anhydride. Industrial V-P-O catalysts capable of activating paraffins for partial oxidation are typically prepared in alcohol solution<sup>1</sup> and contain the unusually active and selective B-phase.<sup>2,3</sup> This study utilizes in situ infrared spectroscopy to probe the mechanism for n-butane selective oxidation on a V-P-O industrial catalyst possessing a slight "excess" of phosphorus (P/V = 1.1) that contains the B-phase.<sup>4</sup>

Relatively simple reaction pathways for *n*-butane selective oxidation to maleic anhydride have been proposed in the literature. The reaction schemes offered by Escardino et al.<sup>5</sup> and Wohlfahrt and Hofmann<sup>6</sup> proposed the direct formation of maleic anhydride from n-butane without mention of reaction intermediates. The combustion of *n*-butane and maleic anhydride to CO, CO<sub>2</sub>, and water occurred according to parallel reactions:



In contrast to the simple reaction pathways offered for paraffin selective oxidation, the reaction schemes for olefin selective oxidation have been relatively complex. The reaction scheme for 1-butene partial oxidation is generally believed to involve 1,3butadiene<sup>7,8</sup> and crotonaldehyde or furan<sup>10</sup> as reaction intermediates. Varma and Saraf<sup>11</sup> offered 1,3-butadiene and possibly furan as reaction intermediates; pathways for the combustion of 1-butene, 1,3-butadiene, and maleic anhydride have also been proposed.



Reaction schemes for the oxidation of 1,3-butadiene to maleic anhydride are believed to involve very reactive peroxide inter-mediates on the catalyst surface.<sup>12,13</sup> Trimm<sup>12</sup> described the addition of a single oxygen molecule to butadiene to form reactive monoperoxides and 2-butenoic acid species; addition of a second oxygen produced maleic acid. The dehydration of maleic acid to maleic anhydride would then follow. Alternatively, the addition of oxygen to butadiene could lead to adsorbed cycloperoxy species which react to give maleic anhydride:12



In previously reported studies,<sup>14,15</sup> in situ infrared spectroscopy has been used to explore the mechanism of n-butane selective oxidation to maleic anhydride. Adsorbed 1-butene, an allylic species or cyclobutene, and maleic acid were observed during the n-butane studies;<sup>14</sup> reactive olefin species and maleic acid were also observed during the 1-butene studies.<sup>15</sup> In this study, crotyl alcohol was used as a mechanistic probe for the formation of reactive olefin species observed previously. Maleic acid and maleic anhydride were fed as probes for adsorbed species identified on the catalyst surface during paraffin and olefin selective oxidation. The use of maleic anhydride feeds also permitted investigation of the combustion mechanism offered by Escardino.<sup>5</sup> Crotonic acid was introduced into the in situ infrared cell as a probe for monoperoxide species which could lead to formation of the acid.

#### **Experimental Procedures**

Catalyst Characterization and Kinetic Measurements. An industrial-type vanadium-phosphorus mixed oxide catalyst having a P-to-V ratio of 1.1 was prepared by the addition of  $H_3PO_4$  to V<sub>2</sub>O<sub>5</sub> reduced in alcohol solution. Characterization of the precipitated, air-calcined, and used V-P-O catalyst was performed by using X-ray diffraction, laser Raman spectroscopy, infrared spectroscopy, and X-ray photoelectron spectroscopy. The synthesis procedure, characterization results, and kinetic measurements for n-butane selective oxidation are reported elsewhere.<sup>2</sup>

In Situ FTIR Cell. The in situ infrared cell described previously<sup>14</sup> was modified by the addition of a syringe injection port

- (1) Hodnett, B. K. Catal. Rev.-Sci. Eng. 1985, 27, 374.
- (2) Wenig, R. W.; Schrader, G. L. Ind. Eng. Chem. Fundam. 1986, 25, 612
  - (3) Cavani, F.; Centi, G.; Trifiro, F. Appl. Catal. 1985, 15, 151.
     (4) Schneider, R. U.S. Patent 3864280, 1970.

  - (5) Escardino, A.; Sola, C.; Ruiz, F. An. Quim. 1973, 69, 385.
  - (6) Wohlfahrt, K.; Hofmann, H. Chem.-Ing.-Tech. 1980, 52, 811
- (7) Ostroushko, V. I.; Kernos, Yu. D.; Ioffe, I. I. Neftekhimiya 1972, 12, 362
- (8) Morselli, L.; Riva, A.; Trifiro, F.; Zucchi, M.; Emig, G. Chim. Ind. (Milan) 1978, 60, 791.
- (9) Ai, M.; Boutry, P.; Montarnal, R. Bull. Soc. Chim. Fr. 1970, 2775. (10) Ai, M. Bull. Chem. Soc. Jpn. 1970, 43, 3490.
  (11) Varma, R. L.; Saraf, D. W. J. Catal. 1978, 55, 361.
- (12) Trimm, D. L. Design of Industrial Catalysts; Elsevier: New York, 1980.
- (13) Margolis, L. Y. Catal. Rev. 1973, 9, 241.
  (14) Wenig, R. W.; Schrader, G. L. J. Phys. Chem. 1986, 90, 6480.
  (15) Wenig, R. W.; Schrader, G. L. J. Phys. Chem. 1987, 91, 1911.

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Figure 1. Crotyl alcohol reaction on P/V = 1.1 V-P-O catalyst at 300 °C: (a) pretreated catalyst at 300 °C; (b) 20 min of reaction; (c) 40 min of reaction; (d) evacuation.

with a high-temperature septum. Catalyst disks (0.1-mm thickness) were formed by using stainless steel dies at a load of 15 000 lbs and were transferred to a stainless steel sample holder within the infrared cell for study. Catalyst pretreatment was accomplished by heating the wafer to 300 °C in a flowing stream of air (75 cm<sup>3</sup>/min). Infrared bands due to residual solvent (1650–1900 cm<sup>-1</sup>) and adsorbed water (1620–1640 cm<sup>-1</sup>) were usually removed.

Vapor Delivery System. Gaseous crotyl alcohol (bp 121 °C), maleic acid (bp 140 °C), maleic anhydride (bp 202 °C), and crotonic acid (bp 185 °C) were fed to the infrared cell by introducing approximately 1 cm<sup>3</sup> of the solid or liquid compounds into an evacuated gas sampling bulb and heating the vessel to near the boiling point. A heated syringe was used to withdraw vapor and to introduce gaseous species into a heated (300 °C) infrared cell. Evacuation of the infrared cell promoted injection of the vaporized feed and prevented the rapid oxidation of the hydrocarbon on the catalyst surface. Air was later fed to selected adsorbates in order to study the formation of oxidized products.

Fourier Transform Infrared Spectrometer. A Nicolet Model 60-SX FTIR spectrometer was used to obtain the infrared spectra. Typically 600 scans were accumulated at 2-cm<sup>-1</sup> resolution with a mercury cadmium telluride (MCT) detector. All spectra presented in this paper were ratioed against single-beam spectra of an evacuated cell at 300 °C with KBr windows. Infrared spectra obtained after the introduction of gaseous feedstocks possessed vibrational bands due to adsorbed species, the catalyst, and gaseous species present in the cell. In situ infrared spectra collected after cell evacuation contained vibrational bands due to adsorbed species and the V-P-O catalyst.

# Results

During previous in situ infrared studies<sup>14</sup> of *n*-butane selective oxidation, reactive olefin species, maleic acid, and maleic anhydride were observed on the V-P-O catalyst surface at 400 °C. In order to further investigate the reaction mechanism for paraffin selective oxidation, the catalyst was exposed to crotyl alcohol, maleic acid, crotonic acid, and maleic anhydride. Reaction temperatures of 300 °C were used in the current oxidation studies in an effort to

observe unusually reactive surface species.

Crotyl Alcohol. The in situ infrared spectra following a 10-cm<sup>3</sup> injection of crotyl alcohol vapor into the evacuated infrared cell are presented in Figure 1. Spectrum 1a was observed for the pretreated P/V = 1.1 catalyst at 300 °C. Spectra 1b was collected 20 min after injection of crotyl alcohol vapor into the infrared cell. A comparison of spectrum 1b with a reference spectra of gaseous crotyl alcohol at 300 °C (Figure 2, spectrum 2a) reveals the nearly complete conversion of crotyl alcohol to butadiene. The formation of butadiene was indicated by C=C stretching vibrations at 1584 and 1603 cm<sup>-1</sup> and by combination bands at 1816 and 1829  $cm^{-1.15}$  Maleic acid species were indicated by a C==O stretching vibration at about 1720 cm<sup>-1</sup>. Vibrational-rotational bands at 2143 and 2350  $\text{cm}^{-1}$  were assigned to CO and CO<sub>2</sub>, respectively. C-H stretching vibrations at 2995, 3030, 3081, and 3105 cm<sup>-1</sup> were assigned to butadiene. After 40 min of reaction (spectrum 1c), additional C-H stretching vibrations due to butadiene were observed at 2864, 2927, and 2970 cm<sup>-1</sup>.

Spectrum 1d was collected following a brief evacuation of the in situ infrared cell. As a result, the infrared bands of gaseous and weakly adsorbed species were removed. A broad C==C stretching vibration from 1570 to 1615 cm<sup>-1</sup> was suggestive of the reactive olefin species observed in *n*-butane<sup>14</sup> and 1-butene<sup>15</sup> oxidation. The broad infrared band in the region 1719–1773 cm<sup>-1</sup> was assigned to the C==O stretching vibrations of maleic acid (1719 cm<sup>-1</sup>) and maleic anhydride (1773 cm<sup>-1</sup>).

Figure 3 provides the in situ infrared spectra following the introduction of 73 cm<sup>3</sup>/min of air into the infrared cell. Spectra 3a, 3b, and 3c were collected after 20, 40, and 60 min (respectively) of air flow. The selective oxidation of adsorbed olefin species to maleic anhydride was indicated by a decrease in the 1570–1615-cm<sup>-1</sup> ( $\nu_{C-C}$ ) olefin band intensity and the appearance of 1778 and 1847 cm<sup>-1</sup> ( $\nu_{C-C}$ ) infrared bands of maleic anhydride. The C=O stretching vibration at 1720 cm<sup>-1</sup> was assigned to maleic anhydride. The C=O stretching vibrations at 2334 and 2362 cm<sup>-1</sup> were assigned to adsorbed CO<sub>2</sub>; surface waters were indicated by a broad 3100–3600-cm<sup>-1</sup> O—H stretching band.

*Maleic Acid.* The in situ infrared spectra following a 10-cm<sup>3</sup> injection of maleic acid vapor are presented in Figure 4. Spectrum



Figure 2. Infrared spectra of (a) gaseous crotyl alcohol; (b) gaseous crotonic acid.



Figure 3. Crotyl alcohol reaction on P/V = 1.1 V-P-O catalyst in air at 300 °C: (a) 20 min of reaction; (b) 40 min of reaction; (c) 60 min of reaction.

4a was observed for the pretreated P/V = 1.1 catalyst at 300 °C. Residual alcohols were assigned to the 1840-cm<sup>-1</sup> band; adsorbed CO<sub>2</sub> was assigned to two bands at 2334 and 2360 cm<sup>-1</sup>. Spectrum 4b was collected following 10 min of maleic acid reaction. Maleic anhydride was assigned to carbonyl stretching vibrations at 1777 and 1849 cm<sup>-1</sup> and by ==CH stretching vibrations at 3124 cm<sup>-1</sup>. Gaseous CO<sub>2</sub> was indicated by vibrational-rotational bands near 2350 cm<sup>-1</sup>. Spectrum 4c was collected 20 min after the injection of maleic acid vapor into the catalytic in situ infrared cell. A decrease in intensity of the 1777- and 1849-cm<sup>-1</sup> maleic anhydride bands and an increase in the intensity of the 2350-cm<sup>-1</sup> CO<sub>2</sub> bands suggested the complete oxidation of maleic anhydride to CO<sub>2</sub>. After 30 min of reaction (spectrum 4d), the further oxidation of maleic anhydride to CO<sub>2</sub> was indicated by very weak C==O stretching vibrations of maleic anhydride at 1777 and 1849 cm<sup>-1</sup> and intense C==O stretching vibrations of CO<sub>2</sub> at 2350 cm<sup>-1</sup>.



Figure 4. Maleic acid reaction on P/V = 1.1 V-P-O catalyst at 300 °C: (a) pretreated catalyst at 300 °C; (b) 10 min of reaction; (c) 20 min of reaction; (d) 30 min of reaction; (e) evacuation.

Maleic acid was assigned to the C=O stretching vibration at 1715  $cm^{-1}$ ; the weak 1628- $cm^{-1}$  infrared band was suggestive of the C=C stretching vibration of maleic anhydride. Adsorbed water was assigned to O-H stretching vibrations in the region 3100-3600  $cm^{-1}$ .

Spectra 4e was collected following a mild evacuation of the infrared cell. As a result, the vibrational-rotational bands of gaseous carbon oxides and weakly adsorbed water were removed. Adsorbed maleic acid was assigned to a C=O stretching vibration at 1715 cm<sup>-1</sup>; adsorbed maleic anhydride was assigned to two C=O stretching vibrations at 1777 and 1849 cm<sup>-1</sup>. Adsorbed CO<sub>2</sub> was also indicated by C=O stretching vibrations at 2350 cm<sup>-1</sup>.

Crotonic Acid. The in situ infrared spectra for the crotonic acid studies with the P/V = 1.1 catalyst are presented in Figure 5. Spectrum 5a was observed for the pretreated V-P-O catalyst at 300 °C. Spectrum 5b was collected 20 min after the injection of crotonic acid vapor into the infrared cell. Infrared bands at 1416, 1441, 1625, 1640, 1681, and 1698 cm<sup>-1</sup> were assigned to crotonic acid by comparison to a reference spectrum of gaseous crotonic acid at 300 °C (spectrum 2b). The C-H bending vibrations of crotonic acid were assigned to the 1416- and 1441-cm<sup>-1</sup> bands; the 1625- and 1640-cm<sup>-1</sup> bands were assigned to C=C vibrations of crotonic acid; the 1681- and 1698-cm<sup>-1</sup> bands were assigned to C=O stretching vibrations of crotonic acid. The infrared band observed at 1779 cm<sup>-1</sup> (spectrum 5b) was assigned to the symmetric carbonyl stretching vibration of maleic anhydride. (The symmetric C=O vibration of maleic anhydride seems to be obscured by a residual solvent band at 1842 cm<sup>-1</sup>.) Gaseous CO and CO<sub>2</sub> were assigned to vibrational-rotational bands at 2143 and 2350 cm<sup>-1</sup>, respectively.

After 40 min of reaction (spectrum 5c) the infrared bands assigned to crotonic acid diminished in intensity while the infrared bands assigned to the C=O stretch of maleic anhydride (1779 cm<sup>-1</sup>) and the vibrational-rotational bands of carbon oxides (2143, 2350 cm<sup>-1</sup>) intensified. In addition, infrared bands were observed at 1725 and 1760 cm<sup>-1</sup>. The 1725-cm<sup>-1</sup> band was assigned to the C=O stretching vibration of an adsorbed maleic acid species. The 1760-cm<sup>-1</sup> shoulder band was not observed during previous in situ studies. After 60 min of reaction (spectrum 5d) the crotonic acid bands at 1625, 1640, 1681, and 1698 cm<sup>-1</sup> lost further intensity while the infrared bands associated with maleic acid, maleic anhydride, CO, and CO<sub>2</sub> increased somewhat in relative intensity.

Spectrum 5e was collected after a mild evacuation of the infrared cell. Adsorbed crotonic acid was assigned to C=C and C=O stretching vibrations at 1620 and 1692 cm<sup>-1</sup>, respectively. Adsorbed maleic acid and adsorbed maleic anhydride were assigned to C=O stretching vibrations at 1720 and 1780 cm<sup>-1</sup>. The 1760-cm<sup>-1</sup> infrared band probably was due to the C=O stretching vibration of a previously unobserved oxidation product.

Maleic Anhydride. The in situ infrared spectra following a 10-cm<sup>3</sup> injection of maleic anhydride vapor are presented in Figure 6. Spectrum 6a was observed for the pretreated P/V = 1.1V-P-O catalyst at 300 °C. A residual solvent band was observed at 1842 cm<sup>-1</sup>; two weak infrared bands at 2334 and 2359 cm<sup>-1</sup> were assigned to C=O stretching vibrations of adsorbed CO<sub>2</sub>. Spectrum 6b was observed 20 min after the introduction of maleic anhydride vapor into the evacuated 300 °C cell. Maleic anhydride was identified by two C=O stretching vibrations at 1777 (shoulder at 1793) and 1847 cm<sup>-1</sup>. Gaseous CO and CO<sub>2</sub> were assigned to vibrational-rotational bands at 2143 and 2350 cm<sup>-1</sup>, respectively. A combination band of maleic anhydride was observed at 3587 cm<sup>-1</sup>. Spectra 6c and 6d were observed after 40 and 60 min of maleic anhydride reaction, respectively. These spectra indicate the oxidation of maleic anhydride to CO and CO<sub>2</sub> on the surface of the V-P-O catalyst.

In spectrum 6e the vibrational-rotational bands of gaseous carbon oxides were removed by an evacuation of the in situ infrared cell. Adsorbed maleic anhydride was assigned to a 1777-cm<sup>-1</sup> C=O stretching vibration; the 1847 C=O vibration of maleic anhydride was obscured by a residual solvent band at  $1842 \text{ cm}^{-1}$ . Adsorbed CO<sub>2</sub> was indicated by two C=O stretching vibrations near 2350 cm<sup>-1</sup>.

# Discussion

The in situ infrared studies of crotyl alcohol, maleic acid, crotonic acid, and maleic anhydride oxidation on a V-P-O catalyst surface were used to investigate the mechanism of maleic anhy-



Figure 5. Crotonic acid reaction on P/V = 1.1 V-P-O catalyst at 300 °C: (a) pretreated catalyst at 300 °C; (b) 20 min of reaction; (c) 40 min of reaction; (d) 60 min of reaction; (e) evacuation.

dride formation from *n*-butane. Crotyl alcohol was used as a mechanistic probe for the formation of reactive olefin species that were observed during previous *in situ* infrared studies.<sup>14,15</sup> Maleic acid and maleic anhydride were fed as probes for previously observed species; furthermore, the introduction of maleic anhydride allowed us to investigate Escardino's<sup>5</sup> combustion mechanism. Crotonic acid was used as a probe for monoperoxide involvement in the stepwise oxidation of 1,3-butadiene to maleic acid.

Crotyl Alcohol. For in situ n-butane oxidation studies,<sup>14</sup> a 1571-cm<sup>-1</sup> infrared band was assigned to the C=C stretching vibration of an allylic or cyclobutene species. A broad 1570– 1615-cm<sup>-1</sup> infrared band was observed during 1-butene oxidation<sup>15</sup> and assigned to adsorbed butadiene and the allylic or cyclobutene species observed in paraffin oxidation. In this study crotyl alcohol was used as a mechanistic probe for the formation of these highly reactive adsorbed olefin species. In a similar study, Burrington et al.<sup>16</sup> found allyl alcohol to be a suitable probe for allylic intermediates during propylene oxidation on bismuth molybdate catalysts. The formation of adsorbed olefin species from crotyl alcohol may involve local structural modifications of the (VO)<sub>2</sub>P<sub>2</sub>O<sub>7</sub> structure.<sup>16</sup>

During the in situ crotyl alcohol studies gaseous butadiene was readily formed by the interaction of crotyl alcohol with the V–P–O catalyst surface. Furthermore, adsorbed and highly reactive olefin species were identified by C==C stretching vibrations in the 1570–1615-cm<sup>-1</sup> region. This study indicates that crotyl alcohol adsorbs to form butadiene (1585–1605 cm<sup>-1</sup>) and reactive allylic or cyclobutene species (1570–1585 cm<sup>-1</sup>) on the catalyst surface. In the presence of oxygen these highly reactive adsorbed olefin species were observed to be readily oxidized to maleic acid ( $\nu_{C=O}$ 1720 cm<sup>-1</sup>) and to maleic anhydride ( $\nu_{C=O}$  1778 and 1847 cm<sup>-1</sup>). Nonselective oxidation products such as CO, CO<sub>2</sub>, and adsorbed

TABLE I: Vibrational Assignments for Crotyl Alcohol Oxidation at 300  $^{\circ}\mathrm{C}$ 

freq, cm <sup>-1</sup>	assignt	species
1570	νς=-ς	methylallyl, cyclobutene
1605	νς=-ς	butadiene
1720	νς=-ο	maleic acid
1778	νς=-ο	maleic anhydride
1847	νς=-ο	maleic anhydride
2143	νς=-ο	carbon monoxide
2350	<sup>и</sup> с=с=0	carbon dioxide
3100-3600	<sup>и</sup> о-н	water

TABLE II: Vibrational Assignments for Maleic Acid Oxidation at 300 °C

<u></u>	freq, cm <sup>-1</sup>	assignt	species
	1715	ν <sub>C=0</sub>	maleic acid
	1777	ν <sub>C</sub> =0	maleic anhydride
	1849	$\nu_{C=0}$	maleic anhydride
	2143	$\nu_{C=0}$	carbon monoxide
	2350	ν <u>ς</u> =ς=0	carbon dioxide
	3100-3600	<sup>р</sup> о—н	water

 $H_2O$  were also observed. Table I summarizes the vibrational band assignments for the in situ infrared spectra of crotyl alcohol oxidation at 300 °C.

Maleic Acid. During the in situ *n*-butane studies<sup>14</sup> adsorbed maleic acid was assigned to a C=O stretching vibration that was observed at 1705-1715 cm<sup>-1</sup>. In these studies an adsorbed maleic acid species was again indicated by an infrared band near 1715 cm<sup>-1</sup>. Furthermore, the dehydration of maleic acid to maleic anhydride and the subsequent combustion of maleic anhydride to carbon oxides and water was readily observed at 300 °C.

This study indicates the maleic acid is a reactive surface species and could be an intermediate in paraffin<sup>14</sup> and olefin<sup>15</sup> selective oxidation to maleic anhydride. Table II summarizes the vibrational band assignments for the in situ infrared spectra of maleic acid oxidation at 300 °C.

<sup>(16)</sup> Burrington, J. D.; Kartisek, C. T.; Grasselli, R. K. J. Catal. 1980, 63, 235.

<sup>(17)</sup> Cavani, F.; Centi, G.; Trifiro, F. J. Chem. Soc., Chem. Commun. 1985, 492.



Figure 6. Maleic anhydride reaction on P/V = 1.1 V-P-O catalyst at 300 °C: (a) pretreated catalyst at 300 °C; (b) 20 min of reaction; (c) 40 min of reaction; (d) 60 min of reaction; (e) evacuation.

Crotonic Acid. In situ crotonic acid studies were undertaken at 300 °C to investigate the possible involvement of crotonic acid species in the stepwise formation of acid groups in the oxidation of butadiene to maleic acid.

The reaction pathway for 1,3-butadiene selective oxidation to maleic anhydride is generally believed to involve the addition of oxygen to form very reactive peroxide species on the catalyst surface.<sup>12</sup> The addition of a single oxygen molecule to butadiene could lead to the formation of monoperoxides and crotonic acid species, before a second addition of oxygen to give maleic acid. The dehydration of acid to maleic anhydride would follow.

$$CH_2 = CH = CH = CH_2 + O_2 \rightarrow H_2C = CH = CH_2OO$$
  
$$H_2C = CH = CH_2OO + RH \rightarrow$$
  
$$H_2C = CH = CH_2OH + R$$



Figure 7 provides a comparison of the in situ infrared spectra for the *n*-butane<sup>13</sup> and crotonic acid studies. Infrared spectra collected during in situ *n*-butane studies (spectrum 7a) revealed C=C stretching vibrations at 1571 and 1650 cm<sup>-1</sup> and C=O stretching vibrations at 1710, 1778, and 1848 cm<sup>-1</sup>. (The 1461-cm<sup>-1</sup> band was assigned to C-H bending vibrations of *n*butane.) Spectrum 7b was collected after 3 h of *n*-butane flow at 400 °C; spectrum 7b was observed after 1 h of crotonic acid reaction at 300 °C. An adsorbed crotonic acid species was identified by C=C stretching vibrations from 1620 to 1640 cm<sup>-1</sup> and by C=O stretching vibrations at 1692 cm<sup>-1</sup> (spectrum 7b).



Figure 7. In situ infrared spectra for the P/V = 1.1 catalyst: (a) 3 h of *n*-butane-air flow at 400 °C; (b) 1 h of crotonic acid reaction at 300 °C.

TABLE III: Vibrational Assignments for Crotonic Acid Oxidation at 300  $^{\circ}\mathrm{C}$ 

freq, cm <sup>-1</sup>	assignt	species	
1441	<sup>у</sup> Он	crotonic acid	
1625	ν <sub>C=C</sub>	crotonic acid	
1640	$\nu_{C=C}$	crotonic acid	
1681	$\nu_{C=0}$	crotonic acid	
1692	$\nu_{C=0}$	crotonic acid	
1715	$\nu_{C=0}$	maleic acid	
1760 <sup>a</sup>	$\nu_{C=0}$		
1778	$\nu_{C=0}$	maleic anhydride	
1848	$\nu_{C=0}$	maleic anhydride	
2143	ν <b>ς</b> =0	carbon monoxide	
2350	ν <u>ο</u>	carbon dioxide	
3100-3600	<sup>и</sup> о—н	water	

<sup>a</sup> Denotes an unidentified oxidation product.

Since the 1620-, 1640-, and 1692-cm<sup>-1</sup> infrared bands of adsorbed crotonic acid were not observed in the in situ *n*-butane studies and since crotonic acid was observed to form "new" adsorbed species not observed previously (1760-cm<sup>-1</sup> shoulder band), crotonic acid does not appear to be an intermediate in paraffin or olefin selective oxidation to maleic anhydride. However, crotonic acid does appear to form maleic acid ( $\nu_{C=0}$  1715 cm<sup>-1</sup>) and maleic anhydride ( $\nu_{C=0}$  1778 and 1848 cm<sup>-1</sup>) on the surface of V-P-O catalysts. Table III provides a summary of the vibrational band assignments for the in situ infrared study of crotonic acid oxidation at 300 °C.

The oxidation of butadiene species to maleic acid without the participation of crotonic acid species makes monoperoxide species unlikely reaction intermediates. However, the addition of oxygen to butadiene could also lead to the formation of cyclic peroxides. The transformation of cyclic peroxide species to maleic acid and maleic anhydride has been proposed.<sup>12</sup>



*Maleic Anhydride*. During the previous in situ paraffin<sup>14</sup> and olefin<sup>15</sup> oxidation studies, infrared bands at 1778 and 1847 cm<sup>-1</sup> were observed on the surfaces of functioning V–P–O catalysts and assigned to the C=O stretching vibrations of adsorbed maleic anhydride. In this study, maleic anhydride vapor was adsorbed onto the catalyst surface at 300 °C, and the C=O stretching vibrations of maleic anhydride were again observed at 1777 and 1847 cm<sup>-1</sup>. Furthermore, this in situ study of maleic anhydride to carbon oxides and water. A summary of vibrational assignments for maleic anhydride oxidation at 300 °C is presented in Table IV.

TABLE IV: Vibrational Assignments for Maleic Anhydride Oxidation at 300  $^{\circ}\mathrm{C}$ 

freq, cm <sup>-1</sup>	assignt	species
1777	ν <sub>C=0</sub>	maleic anhydride
1847	ν <sub>C</sub> =0	maleic anhydride
2143	ν <sub>C==0</sub>	carbon monoxide
2350	<sup>v</sup> c=c=0	carbon dioxide
3100-3600	ν <sub>O=H</sub>	water

# Conclusions

Crotyl alcohol, maleic acid, crotonic acid, and maleic anhydride were found to be reactive species when adsorbed on a V-P-O catalyst at 300 °C. Crotyl alcohol was observed to form conjugated olefin species on the catalyst surface-possibly by interaction with catalyst Lewis acid sites. These adsorbed olefins were identified by C=C stretching vibrations (1570-1605 cm<sup>-1</sup>) assigned to methylallyl, butadiene, or possibly cyclobutene species which were previously observed on the catalyst surface.<sup>7,8</sup> Maleic acid was observed to readily form maleic anhydride and water; furthermore, adsorbed maleic acid was identified by a 1715-cm<sup>-1</sup> C=O stretching vibration that was also observed during the in situ n-butane studies.<sup>13</sup> Crotonic acid was observed to form maleic acid and maleic anhydride on the catalyst surface; however, the C=C (1620-1640 cm<sup>-1</sup>) and the C=O (1680-1692 cm<sup>-1</sup>) stretching vibrations of crotonic acid were not observed during n-butane oxidation. The nonstepwise formation of acid groups suggests the possible involvement of cyclic peroxide intermediates in the transformation of conjugated olefin species to maleic acid. Adsorbed maleic anhydride was identified by two C=O vibrations at 1778 and 1848  $cm^{-1}$  and was readily oxidized to CO and CO<sub>2</sub> at 300 °C.

Since the adsorbed olefin species and maleic acid were identified by the same vibrational frequencies observed for the earlier studies, it seems that olefins and maleic acid could be reaction intermediates in paraffin oxidation. Although crotonic acid did form maleic acid and maleic anhydride, no evidence for crotonic acid participation in the mechanism for *n*-butane selective oxidation was obtained.

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**Registry No.**  $O_2$ , 7782-44-7;  $CO_2$ , 124-38-9; CO, 630-08-0;  $H_2O$ , 7732-18-5; methylallyl, 2154-62-3; cyclobutene, 822-35-5; butadiene, 106-99-0; crotyl alcohol, 6117-91-5; maleic acid, 110-16-7; crotonic acid, 3724-65-0; maleic anhydride, 108-31-6; *n*-butane, 106-97-8; V-P-O, 65506-75-4.