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Heteropolyacid-based catalysts for selective alkane oxidation: mechanism of formation of maleic anhydride from propane

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Abstract

Highly active and selective alkane oxidation catalysts, obtained by heating pyridinium- and niobium-exchanged phosphomolybdate and phosphovanadomolybdate salts under inert atmosphere, can under some conditions lead to maleic anhydride as a major product of propane oxidation. Mechanistic studies based on oxidation of postulated intermediates as well as selectively isotopically labeled propane implicate a route involving oxidative dehydrogenation to propylene followed by acid-catalyzed dimerization to branched C_6 hydrocarbons, the main precursors to maleic anhydride.

Keywords: Acid; Dimerization; Hydrocarbons

1. Introduction

The search for selective catalysts for the direct conversion of light alkanes to oxygenates has attracted a great deal of current research attention, and is well represented in the current issue. Two prime targets are maleic anhydride from butane, the only commercially practiced example to date [1], and acrylic acid from propane. We have recently reported a new catalyst system that achieves selective oxidation of *both* *n*-butane and propane, in contrast to most catalysts that are substrate-specific. Our catalysts, obtained from the Keggin ions PMo_{12} and $PMo_{11}V$, exchanged sequentially with niobium oxalate and pyridine followed by heating to 420 °C in flowing helium, exhibit selectivities that approach and productivities that substantially surpass the best literature values for both of these oxidations [2].

While studying the oxidation of propane we were intrigued to observe that, in addition to forming acrylic and acetic acids, the new catalyst produces substantial amounts of a C_4 product, maleic acid, from a C_3 feed. Under some conditions maleic acid was even found to be the *most* abundant product from propane. We have carried out a series of experiments aimed at elucidating the pathway of this unexpected transformation (and, hopefully, shedding some light on the general behavior of selective alkane oxidation catalysts), and here report our findings.

2. Experimental

Pyridinium- and niobium-exchanged phosphomolybdate and phosphovanadomolybdate catalysts (NbPMo12pyr and NbPMo11Vpyr) were prepared according to our previous report [2]. Propane-1-^{13}C

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of 99% purity, obtained from Isotec Inc., and 1,5-hexadiene (97%) and 4-methyl-1-pentene (98%), obtained from Aldrich, were used without further purification.

Catalytic tests were performed in a fixed-bed continuous-flow reactor (Autoclave Engineers, BTRS-Junior). Before a reaction, the catalyst was pelletized and sieved to 40/60 mesh size (425–600 μm). 200 mg of the catalyst diluted with silicon carbide up to 1 cm^3 were used in each experiment. Immediately prior to reaction, the catalyst was heated to 420 °C for 12 h under flowing helium. Experiments were performed at atmospheric pressure in the temperature range of 340–380 °C with a predetermined molar ratio of hydrocarbon, oxygen, steam and helium carrier. The feed rate of 1,5-hexadiene or 4-methyl-1-pentene was controlled by saturating a helium flow at 0 °C.

Analysis of the products was performed using a gas chromatograph equipped with a mass spectrometer (Hewlett-Packard G1800A). Separation of the products was achieved with a capillary column (Hewlett-Packard HP-Plot Q). Gaseous products were injected into the gas chromatograph using an automated gas-sampling valve and higher boiling point products were collected in an ice-water trap and manually injected.

Quantitative ^{13}C NMR spectra were acquired on a Varian Mercury 300 MHz spectrometer operating at a delay time of 60 s. Samples were prepared in D_2O with the sodium salt of 3-(trimethylsilyl)propionic-2,2,3,3-d_4 acid as reference.

3. Results and discussion

3.1. Formation of maleic acid from propane

The preparation and characterization of the niobium-exchanged phosphomolybdate and phosphovanadomolybdate catalysts have been discussed previously [2]. When properly prepared and activated, these catalysts are extraordinarily active for the selective oxidation of propane and butane; some representative data are shown in Table 1. It should be noted that the feed stream in these oxidations is substantially more hydrocarbon-rich than is typical (although selective oxidation can also be achieved with oxygen-rich feeds, as exemplified by the last entry in Table 1). Under these conditions, as seen in the first two entries 1 and 2, maleic acid[1] is a major (sometimes *the* major) product obtained from propane, indicating that a pathway involving carbon–carbon bond formation competes effectively with “simple” substrate oxidation.

This behavior is not unique to these new catalysts: passing a similar propane-rich feed over a standard VPO butane oxidation catalyst also gives substantial amounts of maleic acid (entry 3). Since oxidation of C_5 and higher hydrocarbons over VPO catalysts is well known to give maleic anhydride as a major product [3,4], a mechanism involving C–C bond formation at a fairly early stage, followed by oxidation (and partial degradation) back down to C_4, appears to be an attractive pathway. Furthermore, since oxidative dehydrogenation is a very probable first step, we have focused on routes for C–C coupling starting with propylene.

3.2. Oxidative coupling of propylene

Under oxidizing conditions, after propane undergoes oxidative dehydrogenation to propylene, generation of allyl radicals followed by coupling to 1,5-hexadiene would seem the most probable route to C_6; there is precedent for that sequence in the literature [5,6]. As a first test of this hypothesis, both proposed intermediates, propylene and 1,5-hexadiene, were subjected to oxidation over the $NbPMo_{11}Vpyr$ catalyst under the same conditions used for propane oxidation. In both cases the major products were maleic and acetic acids, with much less acrylic acid (maleic:acrylic ≈20:1), and smaller amounts of other oxygenated products, including acetone, propionic acid, 4-cyclopenten-1,3-dione, 2-methyl-2-cyclopenten-1-one, 3-methyl-2-cyclopenten-1-one 3-methyl-2,5-furandione and 2H-pyran-2-one. These observations appear fully consistent with the proposal.

To further explore this hypothesis, a more stringent test was devised that makes use of selectively labeled propane ($^{13}CH_3{}^{12}CH_2{}^{12}CH_3$) as an oxidation substrate. First, of course, the appearance of label in C_4 product rigorously rules out any possibility of con-

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[1] We presume that the actual product of oxidation is maleic anhydride, but our analytical procedure, which involves trapping condensable products (along with all the water fed and produced in the reaction) in a cold trap, leads to hydrolysis.

Table 1
Oxidation of propane and butane

Substrate	Catalyst	Flow rate (ml/min)[a]	Conversion[b] (%)		Selectivity[b] (%)				Yield (%)	STY[c]
			HC	O_2	CO_x	Ac	AA	MA		
Propane	$NbPMo_{11}V(pyr)$	8:4:8:10[d]	25[e]	99	15	19	21	43	5.3[f]	0.180[f]
	$NbPMo_{11}V(pyr)$	32:16:32:40[d]	21	69	8	24	50	16	10.5[f]	0.623[f]
	VPO	8:4:8:10[d]	2	10	16	15	13	12	0.3[f]	0.003[f]
Butane	$NbPMo_{11}V(pyr)$	32:16:32:40[d]	14	95	9	5	3	80	11.2[g]	0.760[g]
	$NbPMo_{11}V(pyr)$	1:10:35:5[h]	62	61	50	3.8	0.8	46	28.5[g]	0.019[g]

[a] Hydrocarbon:oxygen:helium:water.
[b] Abbreviations: (HC) hydrocarbon; (CO_x) carbon oxides; (Ac) acetic acid; (AA) acrylic acid; (MA) maleic acid.
[c] STY: mmol acid s^{-1} g^{-1} of catalyst.
[d] 380 °C.
[e] Theoretical maximum conversion.
[f] Acrylic acid.
[g] Maleic acid.
[h] 340 °C.

tamination as an explanation for the results (the same reactor system was used for studies of both butane and propane oxidation). Beyond that, though, the pattern of appearance of label in the product(s) can be compared to the specific predictions of this or an alternate mechanism.

The ^{13}C NMR of the mixture of trapped products is shown in Fig. 1. Several points are notable:

(i) Major peaks are readily assignable to maleic, acrylic, and acetic acids, with a smaller peak around 85 ppm due to (hydrated) formaldehyde,

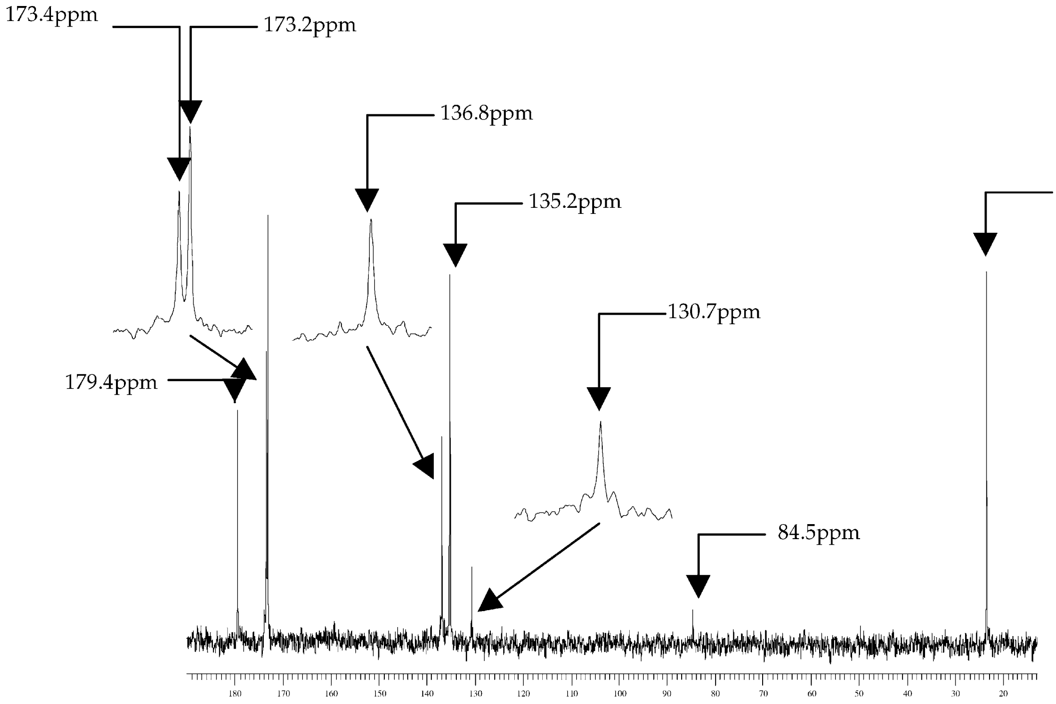


Fig. 1. ^{13}C NMR spectrum of the reaction products of propane oxidation.

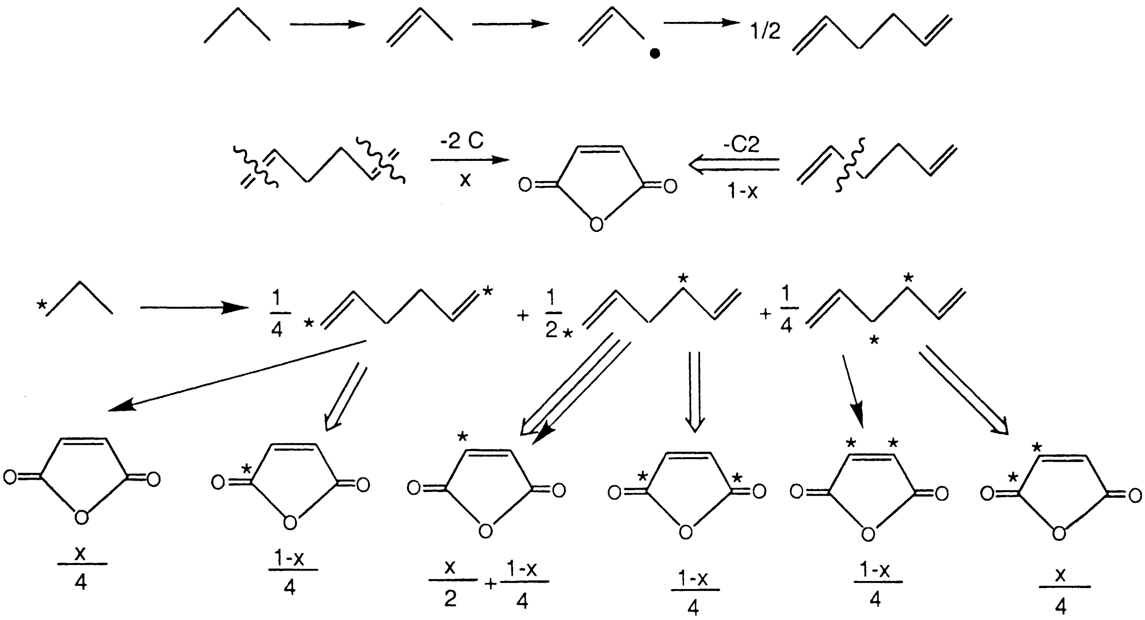
a minor additional propane oxidation product that was not detected by GC/MS. The maleic acid peaks (^{13}COOH, δ 173.4; ^{13}CH, δ 136.8) are comparably intense to those for acrylic acid (^{13}COOH, δ 173.2; ^{13}CH$_2$, δ 135.2) and acetic acid (^{13}COOH δ 179.4; ^{13}CH$_3$, δ 23.4), showing that most or all of the maleic acid does indeed arise from (labeled) propane and not a contaminant.

(ii) The intensities of the two maleic acid peaks are equal, within experimental error, and after correcting for the different relaxation behavior of the carboxylic and olefinic carbon nuclei (determined from the spectrum of a natural abundance sample under identical acquisition conditions).

(iii) In addition to the signals for the two terminal carbons of acrylic acid, which again are equal (after correction) within experimental uncertainty, there is a substantially weaker peak corresponding to ^{13}C at the central position (^{13}CH, δ 130.7).

Up to this point the results of the labeling experiment appear fully consistent with the proposed mechanism. However, on closer examination, difficulties appear. Scheme 1 shows the predicted isotopomeric distribution for maleic anhydride. According to this mechanism there are two possible cleavage patterns that would lead to maleic anhydride: one carbon lost from each end (indicated by a single arrow) versus two carbons lost from one end (double arrow). The relative labeling of the carboxylic and olefinic carbons will depend on the relative frequency of these two paths, assigned values of x and $1-x$ respectively. Summing up, the ratio of total label in the carboxylic and olefinic positions is $(1-x)$:$(x/2+1/2)$. Hence the observed result, that the two positions are approximately equally labeled, implies that $x \approx 1/3$.

But there are additional features of the isotopic distribution that may be tested. Note that, in Scheme 1, a significant fraction of the maleic molecules should have label in adjacent non-equivalent positions (HOOCCH=^{13}CH^{13}COOH). Hence the two ^{13}C NMR signals for maleic should each exhibit satellites due to C–C coupling, centered around the main peak and separated by about 70 Hz [7]. For $x = 1/3$, the intensity of the satellites is calculated to be 1/4 of the total for each signal. As can be seen in the inset to Fig. 1, there are satellites at the expected shifts ($J \approx 65$ Hz), but they are only slightly above the noise level, and



Scheme 1.

contain no more than 5–10% of the intensity of the signals for each position.

The same problem holds for acrylic acid. Most of the acrylic acid is presumably obtained by direct oxidation of propane and hence is labeled only (and equally) in the two terminal positions; but since some acrylic is found during oxidation of 1,5-hexadiene, it would arise as shown in Scheme 2, by cleaving off two carbons from one end and one from the other. (Hexadiene could also cleave in the middle to give acrylic, of course; but the pattern thus produced is the same as that obtained by direct oxidation of propane: terminal label only.) This predicts some label should be found in the central position, as observed; but the predicted isotopomer distribution would require fully half the intensity of that signal to appear in the satellites. In fact, as seen in Fig. 1, no satellites of the central carbon signal are observed above the noise level. (The apparent small peaks flanking the signal at δ 130.7 are separated only by about 30 Hz, and are most probably just noise; the coupling of the carboxylic carbon to the central olefinic carbon has been reported to be 70.4 Hz [8] and the coupling between the two olefinic carbons in methacryclic acid is about the same [7].)

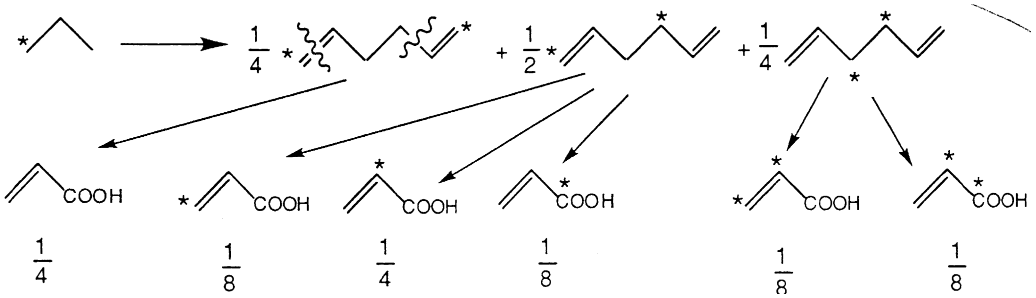
Still another discrepancy arises from mass spectrometry. The mass spectrum of the maleic product obtained from labeled propane shows a substantial fraction of unlabeled and dilabeled molecules; the ratio of ${}^{13}C_0$:${}^{13}C_1$:${}^{13}C_2$ is about 30:45:25. The predicted ratio according to Scheme 1 would be 1:6:5. A distribution of 1:2:1, within experimental uncertainty of the observed values, could be accommodated by this mechanism if all maleic arose by oxidative cleavage of both ends of the hexadiene ($x = 1$); but in that case there would be no label in the carboxylic carbons.

3.3. Cationic dimerization of propylene

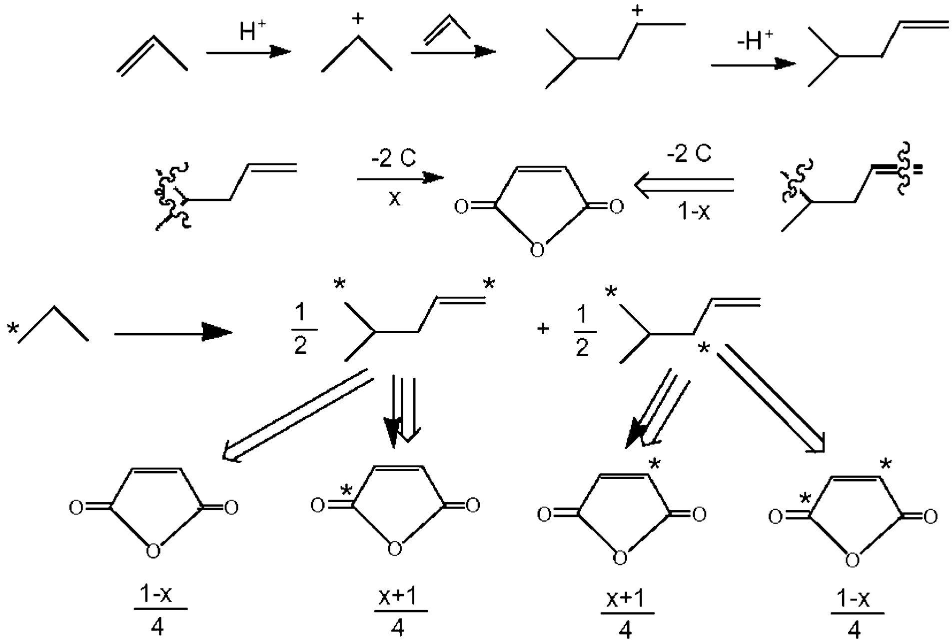
An alternative to the above sequence would be acid-catalyzed dimerization of propylene. We initially considered this less probable, as the overall chemistry involved is oxidative, but there is of course no reason why the catalyst could not have acidic properties as well. Such a mechanism would be expected to lead to primarily *branched* C_6 products, as shown in Scheme 3, with two possible subsequent routes to maleic: cleavage of both methyl groups from the branched end (single arrow), or one of those along with the terminal carbon on the other end (double arrow).

As above, this proposal was tested by feeding 4-methylpent-1-ene. That gives a similar product distribution: maleic and acetic acids are the largest products, but there is relatively more acrylic acid obtained than from 1,5-hexadiene (maleic:acrylic ≈ 10:1). As a further test, propylene was fed in the absence of oxygen. Since the proposed dimerization mechanism is not oxidative, it should proceed without oxygen, and any intermediate hydrocarbons (they are not detected during propane oxidation, presumably being considerably more reactive) should survive. When dry propylene was fed there was little reaction at all; but when propylene plus steam is fed, 4-methylpent-1-ene was indeed produced (along with several other C_6 hydrocarbons including 3-methylpent-2-ene, 2-methylpent-1-ene, 4-methylpent-2-ene, hex-2-ene and 3-methylenepentane) and a number of oxygenates (acetaldehyde, acetone, propanal, acetic acid and propionic acid) in very small amounts, although under these conditions conversion of propylene was fairly low.

The labeling pattern expected from this mechanism is shown in Scheme 3. Note in particular that there



Scheme 2.



Scheme 3.

are no isotopomers that have adjacent labeled carbons, which would also be the case for acrylic acid produced by this route. Furthermore, labeling of the carboxylic and olefinic carbons should be 1:1 independent of the relative probability of the alternate degradation routes. The mass spectrometric distribution of labeled products ($^{13}C_0$:$^{13}C_1$:$^{13}C_2$) suggests that the route involving loss of one carbon from each end predominates (i.e. $x = 0$); that predicts a 1:2:1 distribution, reasonably consistent with the observed values.

4. Conclusions

While maleic acid is obtained as a major oxidation product from either 1,5-hexadiene or 4-methylpent-1-ene (and, we would guess, every other aliphatic C_6 hydrocarbon), the results of the labeling study demonstrate that the major pathway must be via a branched C_6 intermediate, not a linear one. The fact that the ^{13}C NMR resonance for maleic do show some satellite intensity may indicate that some product arises via the linear intermediate produced by competing oxidative dimerization. However, it must also be noted that dimerization of propylene in the absence of oxygen gave not only some linear dimer but also some 3-methylpentenes, which presumably arise via carbonium ion rearrangements. Such rearrangements would produce some C_6 molecules with adjacent labeled carbons and, hence, some satellite signals. At this point these alternatives cannot be distinguished with any confidence. The fact that the satellites are considerably stronger for the maleic peaks than for the central carbon of acrylic may be understandable from the observation that substantially more acrylic (relative to maleic) is obtained from the branched than the linear isomer of C_6; that would tend to support the first alternative.

Acid-catalyzed dimerization of propylene seems the most probable route to branched C_6 intermediates. The fact that only moderate conversion of propylene was observed (and none at all in the absence of added water) would suggest that catalyst acidity is dependent on both oxidation state and the presence of water; we are currently designing experiments to test that possibility. The small amounts of oxygenates obtained under these conditions presumably arise via partial reduction of the catalyst with transfer of lattice oxygens to carbon.

Our findings suggest that the possibility of C–C bond forming reactions should be considered as an alternative to intramolecular rearrangements in accounting for results such as the label scrambling observed in butane oxidation over VPO [9]. While a detailed mechanistic explanation for the selectivity of these novel oxidation catalysts will require a great deal of further work, we can offer at least some tentative conclusions: (1) at least one mobile intermediate must be involved, to permit dimerization (by whatever mechanism); (2) while acidic character has often been considered undesirable for selective oxidation, that is apparently not the case here; (3) a close geometric fit between surface and reactant/intermediate/product structures, as have been proposed to account for the success of VPO as a butane oxidation catalyst, does not seem indicated here. How generally applicable are these conclusions remains to be determined.

Acknowledgements

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