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Investigation of the Mechanism of Catalytic Oxidation of Propylene to Acrolein and Acrylonitrile*

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Deuterated propylene (96% 1-propene-3*d* with 4% ordinary propylene) was selectively oxidized with molecular oxygen in the vapor phase over two catalysts, cuprous oxide and bismuth molybdate, to acrolein, and in the presence of ammonia, to acrylonitrile. There was considerable retention of deuterium in both products. With the cuprous oxide catalyst, 61% of the acrolein formed at 350°C was monodeuterated and 1.3% dideuterated, while 41% of the acrylonitrile formed at 410°C was monodeuterated and 2.9% dideuterated. With the bismuth molybdate catalyst at 450°C, 62% of the acrolein was monodeuterated and 1.6% dideuterated, while 44% of the acrylonitrile was monodeuterated and 0.3% dideuterated. These results suggest that the mechanism of propylene oxidation in these two catalyst systems is the same.

A mechanism consistent with these data involves the formation of an allyl intermediate by abstraction of a hydrogen or deuterium from the methyl group, followed by further abstraction at either end of this symmetric intermediate. The isotope discrimination effect k_D/k_H, assumed to be the same for all the abstractions, was calculated to be 0.58 (ex acrolein results) and 0.49 (acrylonitrile) for the cuprous oxide, and 0.50 (acrolein) and 0.49 (acrylonitrile) for the bismuth molybdate. The constancy of these results indicates that the same mechanism is inherent in the formation of both products.

INTRODUCTION

The oxidation of propylene to acrolein over cuprous oxide has been known for some time (*1*), and the use of bismuth molybdate type catalysts for the formation of acrolein and of acrylonitrile has recently been described (*2*). Little work has been done on the mechanism of these rather unusual and important reactions. The kinetics over cuprous oxide have been found to be first order in oxygen and independent of propylene (*3*). Margolis and co-workers (*4*) measured the change in work function of cuprous oxide when the various reactants were adsorbed and concluded that adsorbed oxygen is negative while adsorbed propylene and various products have a partial positive charge. This group concluded that propylene is adsorbed with the methyl group onto a molecular oxygen ion without breaking the double bond and gives a hydroperoxide, which decomposes into acrolein and water. However, these conclusions are based on adsorption measurements and analogies with homogeneous oxidation with molecular oxygen. Voge, Wagner, and Stevenson (*5*) in a companion paper describe the results of oxidation of C^{13}-marked propylene over cuprous oxide and conclude initial removal of a hydrogen atom from the methyl group occurs to form a symmetrical intermediate that is subsequently oxidized on either end. Propylene oxide was eliminated as an intermediate. This present report summarizes the results of oxidation of 1-propene-3*d* over the two catalyst systems, copper oxide and bismuth molybdate.

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EXPERIMENTAL

All of the data were obtained using a flow system at atmospheric pressure with a single pass of the feed gases over 1 to 2 cc of catalyst. The reactor consisted of a 14 mm ID Pyrex glass tube containing a concentric thermowell running the 6 cm length of the catalyst bed. This reactor was loaded with 10–20 mesh granules of catalyst diluted to 6 cc with Pyrex glass chips of the same size. The feed gases were metered separately and mixed prior to entering the reactor. Typical feed compositions, space velocities, and temperature conditions used for the formation of acrolein and acrylonitrile from the marked propylene are shown in Table 1. These conditions are probably not the optimum ones for these catalysts, but were conveniently close to those described in the literature.

TABLE 1
TYPICAL REACTION CONDITIONS—SINGLE PASS

Catalyst	Copper oxide		Bismuth molybdate	
Major product	Acrolein	Acrylonitrile	Acrolein	Acrylonitrile
Feed ratios (molar)	5 C_3H_5D:1 O_2 :4 He	5 C_3H_5D:1 O_2 :2.5 NH_3 :4 He	1 C_3H_5D:1 O_2 :4 He	1 C_3H_5D:1.8 O_2 :1.5 NH_3 :3.2 He
Total GHSV[a]	1200	750	1800	2150
Temp (°C)	360	410	450	450

[a] Total gas hourly space velocity, basis feed gas volumes at 25°C and 760 mm, per volume of undiluted catalyst.

TABLE 2
DEUTERIUM CONTENT OF PRODUCTS OBTAINED WITH COPPER OXIDE

Compound	Temperature (°C)	Propylene conversion (%)	Deuterium content (%)		
			d_0	d_1	d_2
Propylene feed	—	—	4.3	95.6	0.1
Unreacted propylene[a]	350	7	5.0	94.8	0.2
Acrolein	350	12	37.8	60.8	1.3
Acrylonitrile	410	6	55.9	41.2	2.9

[a] Infrared analysis indicated negligible isomerization.

The copper catalyst was made by the slow deposition of copper onto 10–20 mesh granular SA-101 Alundum (a low surface area bonded alpha alumina) by reduction of an ammoniacal cupric acetate solution with hydrazine to give about 5% copper on the support. The bismuth molybdate was precipitated from an ammonium molybdate solution by addition of bismuth nitrate and ammonia to give a bismuth-to-molybdenum ratio of 1:1. Both catalysts were well washed with water, dried, then calcined at about 450°C prior to use.

The deuterium-labeled propylene was kindly prepared by C. D. Wagner of this laboratory by the method of Hurd *et al.* (*6*). Allyl chloride was allowed to react with zinc and acetic acid-*d* dioxane solution to give a yield of 97% propylene based on the acid. The isotopic and chemical purities as determined by infrared and mass spectrometric analysis were found to be satisfactory.

The exit gases from the reactor flowed past a heated capillary leak through which continuous sampling of the products could be made to a mass spectrometer. The exit gases were also passed through a 40 cc sampling loop of a gas chromatograph, and the separated products trapped from the exit stream of the chromatograph as they passed through a liquid-nitrogen-cooled

U-tube. Spectra at various low ionization voltages were obtained on these trapped fractions and the results plotted to insure that fragmentation was not occurring. The spectra were corrected for natural isotopes, and ionization efficiencies for the various deuterated isomers of the same compound were assumed equal.

TABLE 3

Deuterium Content of Products Obtained with Bismuth Molybdate at 450°C

Compound	Propylene conversion (%)	Deuterium content (%)			
		d_0	d_1	d_2	d_3
Propylene feed	—	4.3	95.6	0.1	—
Unreacted propylene[a]	56	12.3	82.0	5.7	0.1
Acrolein	39	35.6	62.5	1.6	0.4
Acrolein[b]	81	33.3	64.1	2.6	0.2
Acrylonitrile	38	56.1	43.9	—	—
Acrylonitrile[c]	~60	56.1	43.5	0.3	—

[a] Infrared: *trans* 1-*d* and ordinary propylene about 5–20% each. Therefore, isomerization small.

[b] Infrared: About 45% of deuterium on aldehyde group. Bulk of remaining deuterium on terminal carbon of olefin group.

[c] Infrared: Two deutero-isomers. May be *cis* and *trans* on end carbon atom.

Isotopic analysis of the products from copper oxide are given in Table 2 while those from bismuth molybdate are given in Table 3. Data are given in Table 4 on the mass spectra of the acrolein formed with the bismuth molybdate catalyst when various amounts of acrylonitrile are formed. The 56/57 ion ratio is constant within experimental error, indicating that the formation of acrylonitrile does not alter the isotopic composition of the acrolein remaining.

TABLE 4

Isotope Content of Acrolein when Various Amounts of Acrylonitrile are Formed[a]

Run	Ratio acrylonitrile/ acrolein in product	Acrolein 56/57 ion ratio, 70 volts
1	0	0.97
2	0	0.97
3	0	0.98
4	0.55	0.98
5	3.1	1.00
6	8.5	1.00

[a] Bismuth molybdate catalyst, propylene conversion 38–40%, various amounts of ammonia added.

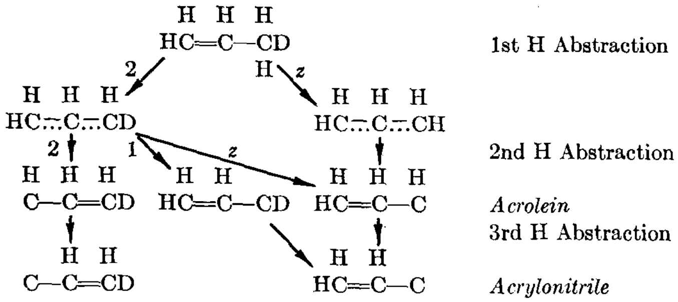
Discussion

The results presented in Tables 2 and 3 immediately give information concerning the mechanism of propylene oxidation in these systems. First, the two catalysts give essentially the same results for isotopic distribution, indicating that the path of reactions to acrolein and acrylonitrile is the same over the two catalysts. Second, the distribution of the deuterium between only the two end carbons in acrolein eliminates the formation of any cyclic C_3 intermediate, and, together with the presence of substantial amounts of deuterium in acrylonitrile, immediately eliminates oxidation exclusively on the methyl group of vinyl position. The data of Tables 2 and 3 (infrared analysis and constancy of isotopic distribution with conversion) also eliminates the possibility of propylene isomerization as the means for exposing either end of the molecule.

The only plausible model which gave a consistent fit to the data was one in which the initial oxidative attack occurs on the methyl group to remove one hydrogen. This leads to a CH_2CHCH_2 species (ignoring isotopes for the moment) which would have a sufficiently labile electronic structure, whether charged or not, that the distinguishability of the end groups will be lost. Further abstractions of hydrogen may therefore occur at either end.

The data obtained in this study provide no evidence for the mechanism by which either oxygen or nitrogen enters the molecules. In the absence of such information, the model will be treated simply as one involving hydrogen abstractions, the product acrolein being identified with the CH_2CHCH species and acrylonitrile with the CH_2CHC species.

The abstraction of deuterium will not necessarily occur with the same probability as that of protium. Further, it is extremely probable that these abstractions are sequential within the same molecule and isotropic discrimination may occur at each abstraction, and will be independent of any kinetic slow step. The detailed electronic structures for the various species involved in the sequential abstractions will undoubtedly be different, but the relative probability for abstraction of deuterium to that of protium for a given step should be approximately constant for all three steps if the same abstracting agent is operative in the various steps. If we let $z = k_D/k_H$ represent this relative discrimination probability, we may write the following reaction path scheme for 1-propene-3*d*.



Here the numbers show the relative probability of the preceding species reacting along the indicated path. It is assumed that these abstractions are not reversible. The data of Table 4 show that the isotopic composition of acrolein is constant, independent of the amount of acrylonitrile formed. This means that there is no kinetic isotope effect in the third step, and the previous steps are independent of the kinetics since the model considers only steady state conditions and only those molecules that do react.

The isotopic compositions from this scheme are as follows:

Acrolein

$$d_0 = \frac{2}{2+z}\cdot\frac{z}{3+z} + \frac{z}{2+z} = \frac{5z+z^2}{6+5z+z^2}$$

$$d_1 = \frac{2}{2+z}\cdot\frac{3}{3+z} = \frac{6}{6+5z+z^2}$$

whence

$$z = -2.5 + \sqrt{0.25 + 6/d_1}$$

Acrylonitrile

$$d_0 = \frac{2+5z+z^2}{6+5z+z^2}$$

$$d_1 = \frac{4}{6+5z+z^2}$$

whence

$$z = -2.5 + \sqrt{0.25 + 4/d_1}$$

Two factors must be considered before the data of Tables 2 and 3 can be applied: the presence of 4.3% ordinary propylene impurity in the feed propylene, and the effect of small amounts of exchange and isomerization. Fortunately, the rate of oxidation of ordinary propylene was sufficiently similar to that of 1-propene-3*d* that this small amount of ordinary propylene may be considered to react at the same rate as the deuterated propylene. Hence, the data may be corrected simply for 4.3% d_0 in the products. It is not so easy to correct for the effects of exchange and isomerization. Several schemes have been considered, each of which affects the results slightly, but none was completely satisfactory. Consideration of the data of Table 2 indicates that exchange is occurring with the products and not with the propylene over cuprous oxide. The data are not so

	Temp (°C)	d_0	d_1	$z = k_D/k_H$	
		Acrolein			
Copper oxide	350	0.350	0.650	0.58	
Bismuth molybdate	450	0.327	0.673	0.53	0.50
Bismuth molybdate	450	0.302	0.698	0.47	
		Acrylonitrile			
Copper oxide	410	0.539	0.461	0.49	
Bismuth molybdate	450	0.541	0.459	0.49	
Bismuth molybdate	450	0.541	0.459	0.49	

clear cut with bismuth molybdate, but exchange of the propylene should lead to the formation of more d_0 product than d_2 product. This does not seem to occur. Exchange in the product, however, would result in three reactions:

$d_1 \rightarrow d_2$; $d_1 \rightarrow d_0$ and $d_0 \rightarrow d_1$

The net effect would be mainly a build-up of d_2 from d_1. In the absence of a completely satisfactory way of treating exchange, the data were somewhat arbitrarily treated as follows:

(a) everything higher than d_1 was considered as being derived from d_1 and considered as d_1, and

(b) the net loss or gain of d_0 was ignored.

Using the above considerations, the following effective composition of products and calculated z values from pure 1-propene-3d were derived.

Considering the uncertainties involved with the multiple exchange, these k_D/k_H values are in quite good agreement. They are also reasonable when compared in Fig. 1 with some approximate theoretical calculations of Melander (*7*) on the values of k_D/k_H to be expected for abstraction from a carbon atom when all three hydrogen vibrations are lost in the transition state. The agreement is good except for the value

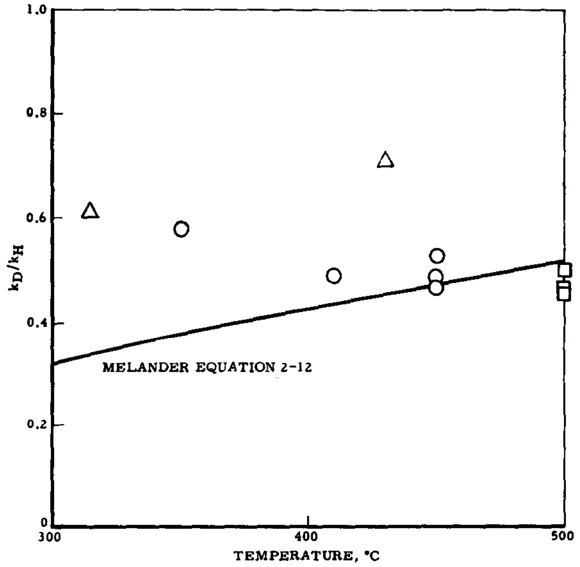


FIG. 1. Calculated k_D/k_H values from the oxidation of deuteropropene (circles) compared to theoretical values [line, ref. (*7*)], ethyl radical decomposition on nickel [triangles, ref. (*8*)] and ethyl chloride, bromide, and acetate pyrolysis [squares, ref. (*9*)].

for acrolein on cuprous oxide at 350°C. This value appears to be too high, and there are several possible causes of this (e.g., localized hot spot temperatures, inaccuracies in dealing with the multiple exchange, not quite complete equilibration of the allyl intermediate, etc.) but we have no reason now for choosing a correction. This comparison with Melander's theoretical results is not to be taken as implying that the details of the transition state for hydrogen abstraction are known, only that the values calculated from the assumed model are physically realistic.

Also shown in Fig. 1 are some values of kinetic isotopic effects observed in the decomposition of ethyl radicals on nickel (*8*) and in the pyrolysis of ethyl chloride, bromide, and acetate (*9*).

The constancy and reasonableness of these results indicates that the same mechanism is inherent in the formation of both acrolein and acrylonitrile over both catalysts. Initial abstraction occurs at the methyl group, forming a symmetric (in terms of further activity) allylic intermediate followed by subsequent abstractions which have the same discrimination factor for deuterium versus hydrogen. This concept of adsorbed allyl radicals is not a new one. Burwell and co-workers (*10*) proposed the allyl radical or ion as a possible intermediate in the reactions between hydrocarbons and deuterium on chromium oxides, while Kemball and co-workers (*11*) have proposed a π-bonded allylic intermediate in the deuterium exchange of paraffins on metal films. It must be mentioned again that these studies do not reveal any details on the mechanism by which oxygen or nitrogen enters the molecules.

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