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Mechanism Studies of the Catalytic Oxidation of Propylene

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Rates of oxidation of various deuterated propylenes over bismuth molybdate show that the rate-determining step is hydrogen abstraction from the methyl group, with a kinetic isotope effect of $k_D/k_H = 0.55$ at 450°C. Percentage retentions of deuterium in the acrolein and acrylonitrile products from 1-propene-1*d* over both bismuth molybdate and cuprous oxide, after reasonable corrections for propylene isomerization and deuterium exchanges, are in agreement with a model in which allylic hydrogen abstraction occurs to form an allylic intermediate followed by hydrogen abstractions from either end. The isotope effect calculated from these retentions agrees with that of the kinetic isotope effect. The results indicate that the allylic intermediate is attacked at a hydrogen atom rather than at a carbon atom. Oxidation of a deuterated butylene to butadiene over bismuth molybdate is in qualitative agreement with the above model.

INTRODUCTION

The vapor phase oxidation of propylene to form acrolein over transition metal oxide catalysts is well known (*1*, *2*). The kinetics over cuprous oxide (*3*) have been found to be first order in oxygen and independent of propylene, while the kinetics over bismuth molybdate type catalysts are first order in propylene and independent of oxygen (*4*). The kinetics of the ammoxidation of propylene with oxygen and ammonia over catalysts of undisclosed composition are reported also to be first order in propylene and independent of the oxygen or ammonia (*5*). Similar kinetics have been found for the ammoxidation of propylene over a bismuth molybdate catalyst (*6*). In a previous paper on the mechanism of these reactions, we reported results obtained in the oxidation of a deuterated propylene (1-propene-3*d*) with molecular oxygen over two catalysts, cuprous oxide and bismuth molybdate, to acrolein, and in the presence of ammonia, to acrylonitrile (*7*). The results suggested that the mechanism of propylene oxidation was the same over both catalysts, and a model consistent with the data was proposed in which the initial hydrogen or deuterium is abstracted from the methyl group to give an allyl intermediate, followed by further abstraction from either end of this intermediate, which is completely symmetrical except for the deuterium marker. The constancy of the isotope discrimination effect, *z*, assumed the same for all abstractions, calculated from the data for the formation of acrolein and of acrylonitrile indicated that the same mechanism is inherent in formation of both products. Here and throughout this paper, the isotopic discrimination effect *z* is the probability of breaking a carbon–deuterium bond relative to that of breaking a carbon–hydrogen bond under the same conditions. Further evidence for the above mechanism of the oxidation of propylene to acrolein over a similar cuprous oxide catalyst has been reported

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using propylene containing a marked carbon atom (*8*). The formation of such a symmetric intermediate has also been confirmed for this oxidation reaction over bismuth molybdate type catalysts using carbon-marked propylenes (*9, 10*). On the other hand, Margolis and co-workers (*11*) concluded that propylene is adsorbed with the methyl group onto a molecular oxygen ion without breaking the double bond to give a hydroperoxide, which decomposes to acrolein and water. These conclusions, however, were based only on adsorption measurements and analogy with homogeneous oxidation mechanisms with molecular oxygen.

In continuation of the earlier study, this report is concerned with:

1. The kinetic isotope effect in the oxidation of propylene over bismuth molybdate.
2. The deuterium distribution in acrolein and acrylonitrile formed from 1-propene-1*d* over bismuth molybdate and cuprous oxide.
3. A detailed study of the side effects of exchange and isomerization occurring in these reactions.
4. Mechanistic considerations of the introduction of oxygen and nitrogen into the intermediates involved.
5. Some semiquantitative data on the oxidation of 1-butene-3*d* over bismuth molybdate.

Experimental techniques will be described where appropriate in the discussion of the various results.

Results and Discussion

Kinetic Isotope Effects

No olefin primary kinetic isotope effect would be expected in the oxidation of propylene over cuprous oxide since the reaction kinetics are zero order in propylene and first order in oxygen over this catalyst (*3*). Over bismuth molybdate, however, the oxidation of propylene is first order in propylene, zero order in oxygen and ammonia (*4, 6*), and should show a kinetic isotope effect. Another study on the oxidation of other olefins over bismuth molybdate has indicated that the kinetic slow step is the abstraction of an allylic hydrogen atom from the olefin (*12*). This step would be expected to show a primary kinetic isotope effect similar, if not identical with, the discrimination isotope effect found earlier (*7*). The rates of oxidation of several deuterated propylenes were therefore examined at constant flow, constant temperature, and low conversions (14–24%) over bismuth molybdate in an apparatus similar to that described previously (*7*). The results are shown in Table 1 in terms of first order rate constants relative to ordinary propylene. The values given are for pure isomers, appropriate corrections having been made for the impurities in the real feeds.

TABLE 1
First Order Rate Constants for the Oxidation of Deuterated Propylenes over Bismuth Molybdate at 450°C

Compound	Rate constant	
	Observed[a]	Calculated
C_3H_6	1.00	(1.00)
$CH_2{:}CHCH_2D$	0.85 ± 0.02	0.83
$CHD{:}CH\ CH_3$	0.98 ± 0.02	1.00
C_3D_6	0.55	0.50

[a] Errors listed are average errors.

The calculated values listed in Table 1 are those obtained by assuming the slow step to be abstraction of an allylic hydrogen with an isotope effect equal to the discrimination effect obtained earlier by consideration of the retention of deuterium in the products from 1-propene-3*d* (*7*). 1-Propene-1*d* showed no kinetic isotope effect, while the rate of oxidation of 1-propene-3*d* agreed well with that expected for initial attack at the methyl group. The observed kinetic isotope effects give independent evidence that the initial and rate-controlling step is attack at the allylic position. The good agreement with the calculated values gives excellent confirmation for the mechanistic scheme proposed.

Location of Deuterium in Product Acrolein

The isotopic distribution in the products obtained on oxidation of 1-propene-3*d* over both bismuth molybdate and cuprous oxide was reported previously (*7*). Through the courtesy of J. Jungnickel and J. Forbes, the hydrogen nuclear magnetic resonance spectra were obtained for the acrolein and acrylonitrile from the oxidation of 1-propene-3*d* over bismuth molybdate at 450°C. Unfortunately, the spectrum of the vinyl group is quite complicated and assignment of locations within it cannot be made at present. However, for the acrolein ($d_0 = 36.8 \pm 0.4\%$; $d_1 = 61.3 \pm 0.4\%$; $d_2 = 1.8 \pm 0.2\%$ by M.S. analysis) the amount of hydrogen in the vinyl group was $77.8 \pm 0.3\%$ of the total hydrogen in the product. From this, $62 \pm 3\%$ of the total deuterium is in the vinyl group. If we correct by making the assumption that the dideuteroacrolein contains one deuterium each in the aldehyde group and the vinyl group, then the ratio of deuterium in the aldehyde group to that in the vinyl group in the monodeuterated acrolein is 0.6 ± 0.1. The proposed mechanism for oxidation would require a value of 0.50 for this ratio, which is in essential agreement.

Oxidation of 1-Propene-1d

This isomer was oxidized to both acrolein and acrylonitrile over cuprous oxide and bismuth molybdate. The reaction system, reaction conditions, and catalysts were the same as those described previously (*7*). The 1-propene-1*d* was kindly prepared by W. L. Petty of this laboratory by decomposing the corresponding Grignard compound with deuteroacetic acid. The Grignard was formed from a mixture of *cis*- and *trans*-1-bromopropenes containing only 0.1% 2-bromopropene. Infrared analysis indicated that deuterated propylene was mainly as the *cis* isomer, with less than 1% 1-propene-3*d* present.

As in the previous study, the exit gases from the reactor were continuously sampled for analysis through a capillary leak to a mass spectrometer. These gases were also sampled through a 40-cc loop of a gas chromatograph and the separated products trapped from the exit stream of the chromatograph in 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 no fragmentation was occurring. The spectra were corrected for natural isotopes, and ionization efficiencies for the various deuterated isomers of the same compound were assumed equal.

A condensation of the results obtained with bismuth molybdate is given in Table 2. Before being examined in detail, these data must be corrected for two side effects, impurity in the feed and the presence of dideuterated product. The kinetic data of Table 1 indicate ordinary propylene and 1-propene-1*d* react at the same rate, so the products can readily be corrected for 12.4% d_0 coming from the ordinary propene in the propylene feed. The second effect is more difficult to correct and we have not yet devised a completely satisfac-

TABLE 2
DEUTERIUM CONTENT OF PRODUCTS OBTAINED WITH BISMUTH MOLYBDATE AND 1-PROPENE-1*d*

Compound	Temp (°C)	Propylene conversion (%)	Deuterium content (%)		
			d_0	d_1	d_2
Propylene feed[a]	—	—	12.4 ± 0.1	87.6 ± 0.1	0.0 ± 0.1
Acrolein	450	63	30.1 ± 0.4	68.4 ± 0.4	1.6 ± 0.1
Acrolein	450	77	30.9 ± 0.5	67.2 ± 0.5	1.9 ± 0.1
Acrylonitrile	455	39	51.2 ± 0.1	48.4 ± 0.1	0.4 ± 0.1
Acrylonitrile	460	75	50.5 ± 0.2	49.0 ± 0.2	0.5 ± 0.1

[a] Infrared analysis indicated less than 1% 1-propene-3*d*.

tory treatment. A detailed consideration of the data obtained in this and the previous work indicated that dideuterated product results more from exchange of the intermediates or product than from exchange of the propene feed. For simplicity, we shall assume exchange of the final product only. All of the acrolein made from the monodeuterated propenes contained approximately 2% d_2 from both catalysts with propylene conversions varying from 4% to 81%. Although this constancy is suspicious, careful examination suggests the d_2 values are real. Possible sources of error, such as abnormal carbon or oxygen isotopic abundances, proton transfer reactions within the mass spectrometer, formation and nonseparation of propionaldehyde or other chemical impurities, or exchange in the separation and trapping facilities, have been carefully examined and rejected. If exchange of product molecules occurs with the surface or some other source of deuterium, then, as argued previously (7), $d_0 \rightarrow d_1$, $d_1 \rightarrow d_0$, and $d_1 \rightarrow d_2$ gives a net effect of $d_1 \rightarrow d_2$. If the product molecules exchange between themselves, however, the net effect will be $d_1 \rightarrow \frac{1}{2}\, d_2 + \frac{1}{2}\, d_0$. Using these two exchange models to correct the data for formation of dideuterated product, d_2, the two sets of corrected data were then used to calculate the amount of isomerization of the two monodeuterated propylenes over bismuth molybdate assuming $z = 0.55$. The amount of isomerization should be about the same for both propylenes under similar conditions, but the calculated amount of isomerization for 1-propene-3*d* was higher than that of 1-propene-1*d* using the experimental data corrected for d_2 according to one exchange model, while the calculated degree of isomerization was reversed when the data were corrected for d_2 by the other exchange model. In order to obtain about the same calculated isomerization for the two propylenes it was necessary to assume about equal contribution of the two modes of exchange to form d_2. In the absence of any other criteria, we have corrected all of the experimental data from this and the previous work (7) for d_2 formation by exchange according to the compromise: $2\, d_1 \rightarrow \frac{3}{2}\, d_2 + \frac{1}{2}\, d_0$. Fortunately, exchange is not large and accounts for an uncertainty in k_D/k_H values calculated from acrolein of less than 10%. Dideuteration is not significant for acrylonitrile. The data of Table 2, corrected for exchange and feed impurity as discussed above, are given in Table 3.

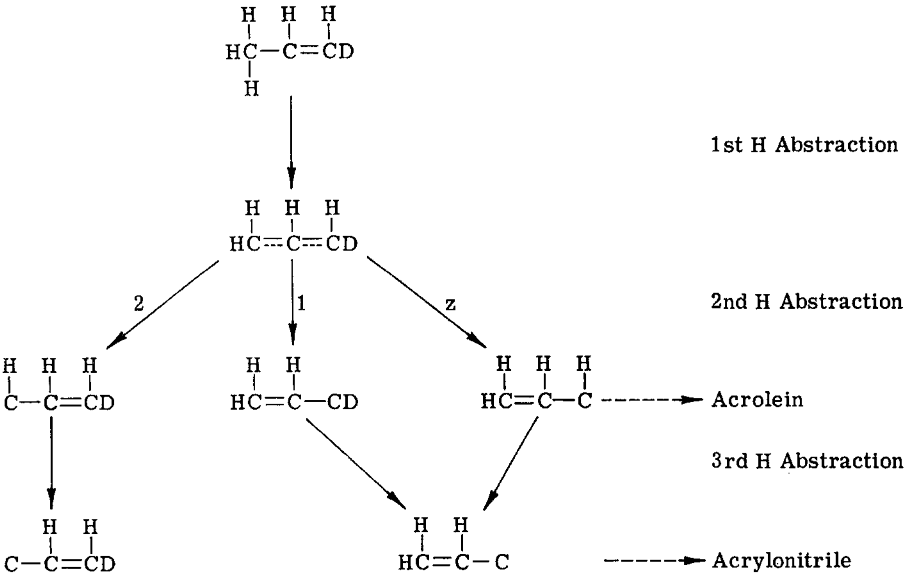
The mechanism proposed, as previously, involves an initial hydrogen abstraction from the methyl group to form an allylic species on the catalyst surface. This is followed by a second abstraction from either end of this symmetrical intermediate to give a species which readily picks up oxygen to yield acrolein. When ammonia is present, attack continues at the same end carbon atom from which the second hydrogen was abstracted, the lone remaining hydrogen is lost and an adsorbed species is formed which readily gives acrylonitrile. Assuming a constant isotope effect, z, in both the first and second abstractions, and since no isotope effect is possible in the third abstraction step, the scheme for 1-propene-1*d* may be written as follows:

TABLE 3

DEUTERIUM CONTENT OF PRODUCTS OBTAINED WITH BISMUTH MOLYBDATE AND 1-PROPENE-1*d*[a]

Compound	Temp (°C)	Propylene conversion (%)	d_0 (%)	d_1 (%)	z
Acrolein	450	63	19.6 ± 0.4	80.4 ± 0.4	0.73 ± 0.02
Acrolein	450	77	20.4 ± 0.5	79.6 ± 0.5	0.77 ± 0.03
Acrylonitrile	455	39	44.2 ± 0.1	55.8 ± 0.1	0.58 ± 0.01
Acrylonitrile	460	75	43.3 ± 0.2	56.7 ± 0.2	0.53 ± 0.01

[a] Corrected for impurities and exchange.



For acrolein:

$$d_0 = z/(3+z),$$
$$d_1 = 3/(3+z),$$
$$z = (3/d_1) - 3$$

and for acrylonitrile:

$$d_0 = (1+z)/(3+z),$$
$$d_1 = 2/(3+z),$$
$$z = (2/d_1) - 3$$

The z values of Table 3 have been calculated in this way. The data obtained previously (7) for oxidation of 1-propene-3d over bismuth molybdate are given in their corrected form in Table 4.

TABLE 4
DEUTERIUM CONTENT OF PRODUCTS OBTAINED WITH BISMUTH MOLYBDATE AND 1-PROPENE-3d[a]

Compound	Propylene conversion (%)	d_0 (%)	d_1 (%)	z
Acrolein	39	32.3	67.7	0.52
Acrolein	81	29.4	70.6	0.46
Acrylonitrile	38	54.1	45.9	0.49
Acrylonitrile	60	54.1	45.9	0.49

[a] Corrected for impurities and exchange, 450°C.

The values for z shown in Tables 3 and 4 calculated from the acrolein data for 1-propene-1d are high and those for 1-propene-3d are low relative to the expected kinetic value of $z = 0.55$, which is as expected if some of the propylene isomerizes before reaction. The data further suggest such isomerization in that divergence increases with propylene conversion or contact time. The extent of isomerization of the reacted propylene that had isomerized before reaction was calculated from the analysis of the acrolein products and assuming $z = 0.55$. These calculated values, assuming $K_{\text{equil.}} = 1d/3d = \frac{2}{3}$, are shown in Fig. 1. Also shown is an infrared analysis of unreacted propylene from one of

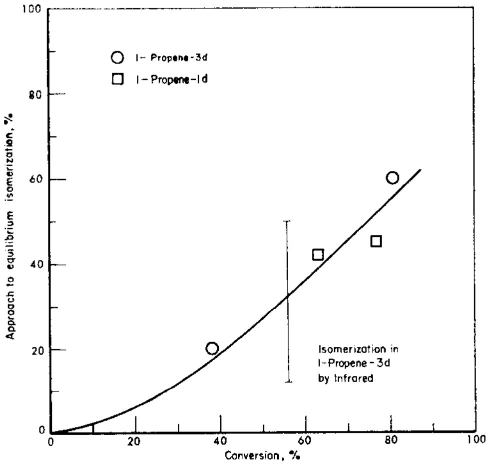


FIG. 1. Calculated amount of isomerization of reacted propylene over bismuth molybdate.

the isomers fed. These values appear reasonable.

The z values calculated from the acrylonitrile data, shown in Tables 3 and 4, agree quite well for the two propylenes over a considerable conversion variation, and so suggest no isomerization occurs in the presence of ammonia. It has been independently shown in these laboratories that olefins do isomerize somewhat over bismuth molybdate during oxidation, and that ammonia inhibits this isomerization.

A summary of the results obtained on the oxidation of 1-propene-1*d* over cuprous oxide is given in Table 5. A large number of values from 1-propene-1*d* were obtained for acrylonitrile and it was found that long contact times led to increased deuterium exchange in the product. The value given in Table 5 was obtained in a short contact time experiment where this effect was minimized.

In Table 6 are given data for both monodeuterated propylenes after correction for feed impurity and dideuteration. The calculated z factors from acrolein agree very well for the two isomers (0.55 and 0.57). These values would be expected to be somewhat lower than this for the temperature measured, but this may be due to local hot spots.

The values obtained for acrylonitrile do not agree, however. In fact, the calculated value of $z = 1.05$ in Table 6 from 1-propene-1*d* is absurd, but the experimental data were reproduced many times and the results are not due to errors in experimental techniques. Further, the data of Table 5 for unreacted propylene show that the effect is not due to exchange of the unreacted propylene. The following experiment was then made. Ammonia, oxygen, and 1-propene-1*d* were passed over the copper catalyst, and the effluent gases, together with added oxygen and ammonia, passed over bismuth molybdate.

The yield of product acrylonitrile from the copper catalyst was negligible compared to that from the bismuth molybdate catalyst, so the acrylonitrile produced from the second reactor represents the reaction over bismuth molybdate of the un-

TABLE 5

DEUTERIUM CONTENT OF PRODUCTS OBTAINED WITH CUPROUS OXIDE AND 1-PROPENE-1*d*

Compound	Temp (°C)	Propylene conversion (%)	Deuterium content (%)			
			d_0	d_1	d_2	d_3
Propylene feed[a]	—	—	12.4 ± 0.1	87.6 ± 0.1	0.0 ± 0.1	—
Unreacted propylene[b]	405	8	13.0 ± 0.3	86.8 ± 0.3	0.2 ± 0.2	—
Acrolein	360	9	27.2 ± 0.4	69.6 ± 0.4	2.1 ± 0.3	1.1 ± 0.2
Acrolein[b]	420	22	29.0 ± 0.7	67.4 ± 0.7	2.7 ± 0.7	0.9 ± 0.1
Acrylonitrile	410	4	56.9 ± 0.2	42.5 ± 0.2	0.6 ± 0.1	—

[a] Infrared analysis indicated less than 1% 1-propene-3*d*.

[b] Ammonia present.

TABLE 6

DEUTERIUM CONTENT OF PRODUCTS OBTAINED WITH CUPROUS OXIDE[a]

Propylene fed	Compound	Temp (°C)	Propylene conv. (%)	d_0 (%)	d_1 (%)	z
1-Propene-1*d*	Acrolein	360	9	15.6 ± 0.4	84.4 ± 0.4	0.55 ± 0.02
1-Propene-1*d*	Acrylonitrile	410	4	50.6 ± 0.2	49.4 ± 0.2	1.05 ± 0.02
1-Propene-3*d*	Acrolein	350	12	34.6 ± 0.6	65.4 ± 0.8	0.57 ± 0.02
1-Propene-3*d*	Acrylonitrile	405	7	55.9 ± 0.3	44.1 ± 0.3	0.55 ± 0.01

[a] Corrected for impurities and exchange (d_2).

reacted propylene from the copper catalyst. It is clearly apparent from the data listed in Table 7 that the propylene leaving the copper catalyst was not the same as the original 1-propene-1*d*. The acrylonitrile formed in the staged reactors had lost considerably more deuterium than that formed over bismuth molybdate. Table 5 showed that little exchange had occurred, so it would appear that the propylene had isomerized. The calculated amounts of isomerization required to fit the observed data were 22% and 41% of the unreacted propylene converted to 1-propene-3*d* at 4% and 7% chemical conversion, respectively, over the copper catalyst. The acrolein data of Table 5 obtained in the presence of ammonia also indicate isomerization. Isomerization accounts for about half the discrepancy between the observed and expected isotopic composition of the acrylonitrile from 1-propene-1*d* over cuprous oxide, the d_0 content still being 3–4% higher than expected. Isomerization should also occur with 1-propene-3*d*. Assuming the same amount of isomerization occurs with 1-propene-3*d* as was calculated for 1-propene-1*d*, the d_0 value for acrylonitrile from 1-propene-3*d* in Table 6 is also 3–4% higher than expected, as were the results from 1-propene-1*d*. The perdeuteropropylene work, described below, showed that ammonia can serve as a source of protons for exchange with acrylonitrile, and so the 3–4% increase in d_0 value above that expected for the two acrylonitriles is probably due to exchange with hydrogen from ammonia.

There is an apparent contradiction here in postulating isomerization over bismuth molybdate only in the absence of ammonia, but over cuprous oxide only in the presence of ammonia. However, ammonia very severely inhibits the oxidation of propylene over copper while it does not inhibit over bismuth molybdate under these conditions (*6*). Thus more severe conditions are required to make propylene react over cuprous oxide on addition of ammonia, as shown by the data of Table 6, where the total gas hourly space velocity was about 300 at 410°C in the presence of ammonia and 1200 at 350–360°C when ammonia was not present, as well as a large difference in temperature. Over bismuth molybdate, ammonia may well neutralize acid sites that are active for isomerization but not for oxidation.

Oxidation of Perdeuteropropene

These experiments were performed using the pulse microreactor technique in which a few milliliters of reaction gas mixture was passed as a pulse at 450°C over a bismuth molybdate catalyst placed in the carrier gas line ahead of a GLC column. Contact times are uncertain due to possible retention of material by the catalyst, so the results can be considered as qualitative only. Propylene conversion was very high

TABLE 7

FORMATION OF ACRYLONITRILE IN STAGED REACTORS[a]

First stage conversion (%)	Second stage conversion (%)	Acrylonitrile composition (%) d_0	d_1	d_2
4	45	53.0 ± 0.3	46.7 ± 0.3	0.2 ± 0.1
7	87	55.0 ± 0.4	44.3 ± 0.4	0.7 ± 0.1
4[b]	—	56.9 ± 0.2	42.5 ± 0.2	0.6 ± 0.1
—	39[c]	51.2 ± 0.1	48.4 ± 0.1	0.4 ± 0.1
—	75[c]	50.5 ± 0.2	49.0 ± 0.2	0.5 ± 0.1

[a] Cuprous oxide at about 405°C in first stage, bismuth molybdate at about 450°C in second stage. 1-Propene-1*d* feed. Yield of acrolein and acrylonitrile from first stage less than 2% of acrylonitrile yield from second stage. Data not corrected for feed impurity.

[b] Second stage omitted, ex Table 5.

[c] First stage omitted, ex Table 2.

(80–100%). When only perdeuteropropene and oxygen were fed, no significant loss of deuterium in the products occurred, indicating that the reservoir of exchangeable hydrogens on the catalyst is small. When ammonia was also fed, up to 25% of the propylene, acrolein, and acrylonitrile molecules picked up a hydrogen atom. When water was fed, some hydrogen pickup occurred, but the amount was much smaller than with ammonia. Although only qualitative, these results indicate that ammonia may serve as a source of exchangeable hydrogen atoms.

Oxidation of 1-Butene-3d

Only small quantities of this butene were available from a preparation kindly made by C. D. Wagner of these laboratories, and so the pulse technique was used here also. The products from the bismuth molybdate catalyst were then passed through a GLC column and the separated fractions trapped for mass spectral analysis. The results are shown in Table 8. The conversion level was varied by using different amounts of catalyst, for varying the helium flow rate over the catalyst by a factor of two had little effect on the butene conversion.

Interpretation of analyses was complicated by impurities in the feed. The data of Table 8 are corrected for the butadiene (99.7% d_0) content of the feed, but the presence of 2-butene was neglected since 1-butene reacts faster.

A model for the dehydrogenation of 1-butene in which the initial extraction of an allylic hydrogen to give a methyl allyl radical, with the second extraction occurring at the methyl group, requires an isotope effect of $z = 0.7$ to fit the data. This compares with the value of 0.55 for the isotope effect in the oxidation of propene at this temperature. However, so many uncertainties were present in the oxidation of butene (butadiene impurity and location of deuterium in the feed, effect of secondary reactions in the pulse technique, etc.) that these results can be considered only qualitative but in agreement with the model.

CONCLUSIONS

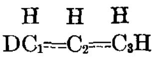
These results give substantiation to the mechanism presented earlier for the oxidation of propylene over bismuth molybdate and cuprous oxide (7). They also give insight to some of the side effects sometimes occurring in these systems. The oxidation of propylene over bismuth molybdate in the presence of ammonia is quite uncomplicated and gives an isotope discrimination effect of 0.49–0.58 in quite good agreement with a kinetic isotope effect of 0.55. Oxidation over bismuth molybdate in the absence of ammonia is complicated by some propylene isomerization, but when reasonable corrections are made the isotope results are in agreement with the other results. Oxidation over cuprous oxide in the absence of ammonia is also uncomplicated, giving a discrimination effect of 0.55–0.57. Oxidation over cuprous oxide in the presence of ammonia is quite complicated by propylene isomerization and apparently by exchange with some form of hydrogen whose source is

TABLE 8
DEUTERIUM CONTENT OF FEED AND PRODUCT[a]

		Product butadiene		
Content	1-Butene fraction of feed	At 11% conv. C_4	At 43% conv. C_4	Unreacted 1-butene frac. at 9% conv. C_4
% Nondeuterated	20.3	55.6	46.8	21.4
% Monodeuterated	79.7	43.2	46.8	78.3
% Dideuterated	0.3	1.2	5.7	0.4
% Trideuterated	—	—	0.7	—
% Tetradeuterated	—	—	0.05	—

[a] Feed composition (by GLC): 1-butene, 88%; 2-butene, 8.5%; butadiene, 3.35%; temperature: 450°C.

ammonia. When these various side reactions are accounted for, the results presented in this study agree quite well with the model involving allyl hydrogen abstraction followed by attack at either end of the allylic intermediate. The data also give further information on the mechanism of attack on the allylic intermediate. Consider the adsorbed species



$$\mathrm{D}\overset{\mathrm{H}}{\mathrm{C}_1}=\overset{\mathrm{H}}{\mathrm{C}_2}=\overset{\mathrm{H}}{\mathrm{C}_3}\mathrm{H}$$

which is an intermediate for both monodeuterated propylenes. The model proposed previously assumed implicitly that further attack occurs through the hydrogen (or deuterium) atoms in that the probability of attack was considered proportional to the reactivity of these atoms. For the reactivities found, attack at C_1 is then about three-fourths as likely as at C_3. It is not inherently obvious that this should be so. In particular, if the reaction of this species occurs by bond formation directly to the carbon atom, essentially equal reactivity would be expected for C_1 and C_3. If equal attack on these *carbon atoms* is assumed with an isotope effect in removal of H or D from C_1, the following relationships may be derived for the products from the two pure monodeuterated propylenes:

1-Propene-1*d*:

Acrolein: $z = 2d_0/(1 - 2d_0)$

Acrylonitrile: No isotope effect, $d_0 = 50\%$

1-Propene-3*d*:

Acrolein: $z = 1/d_1 - 1$

Acrylonitrile: $z = 1/d_1 - 2$

Applying these relationships to the low conversion data of Tables 3 and 4 for bismuth molybdate gives $z = 0.64$ calculated from the observed d_0 of acrolein from 1propene-1*d*, and predicted $d_0 = 50\%$ for the acrylonitrile from 1-propene-1*d*, whereas $d_0 = 44\%$ was observed. For the acrolein from 1-propene-3*d*, the observed d_0 gives $z = 0.48$, while the observed d_0 of acrylonitrile gives $z = 0.18$. Similar results were obtained with cuprous oxide.

The results with acrolein are not very sensitive to the mechanism of the second abstraction, but the results with acrylonitrile are quite sensitive and in complete disagreement with the model of attack directly on the carbon atom. Thus these data indicate quite conclusively that subsequent attack on the allyl intermediate does not occur on a carbon atom, but rather at a hydrogen atom, and suggests that the introduction of the hetero atom (oxygen or nitrogen) occurs after the hydrogen abstraction from the allyl intermediate.

The fact that ammonia inhibits the isomerization of propylene over bismuth molybdate while not inhibiting the oxidation reaction, where the rate-limiting step is abstraction to form the allylic intermediate, indicates that this intermediate has no carbonium ion character. Carbanion character has already been eliminated (*12*), so that the initial abstraction must involve the homolytic scission of the C–H bond.

A recent publication by Sixma, Duynstee, and Hennekens (*13*) on the oxidation of propene-1-C^{14} to acrolein on a copper catalyst has also indicated the presence of a symmetrical intermediate. Sixma *et al.* have criticized our published model (*7*) for having no isotope effect in the abstraction of the last hydrogen for forming acrylonitrile. However, in the absence of hydrogen lability within the whole molecule (and the evidence is quite strong on this point), there can be no isotope discrimination effect in this last abstraction step since the carbon atom going to the nitrile group has only one hydrogen (or deuterium) attached, which must be removed. No kinetic isotope effect is present since all intermediates formed are converted to product. Therefore, the mechanism presented (*7*) requires no isotope effect in the last abstraction for forming acrylonitrile. An alternative model presented by Sixma *et al.*, involving no isotope effect and the formation of the 1,3-diadsorbed CH_2–CH_2–CH_2 intermediate is refuted by the differences in deuterium content of products from 1-propene-1*d* and 1-propene-3*d*, the absence of deuterium on the center carbon atom in the products, and the kinetic isotope effect found for oxidation over bismuth molybdate.

REFERENCES

1. HEARNE, G., AND ADAMS, M., U. S. Patent 2,451,485, 1948 (to Shell Development Company).
2. VEATCH, F., CALLAHAN, J. L., MILBERGER, E. C., AND FORMAN, R. W., *Actes Congr. Intern. Catalyse, 2ᵉ, Paris, 1960* **2**, 2647 (1961).
3. ISAEV, O. V., AND MARGOLIS, L. YA., *Kinetika i Kataliz* **1**, 237 (1960).
4. ADAMS, C. R., VOGE, H. H., MORGAN, C. Z., AND ARMSTRONG, W. E., to be published.
5. LOBKINA, V. V., ABAEV, G. N., SEREBRYAKOV, B. R., AND PLAKSUNOVA, S. L., *Dokl. Akad. Nauk. S.S.S.R.* **145**, 1058 (1962).
6. JENNINGS, T. J., to be published.
7. ADAMS, C. R., AND JENNINGS, T. J., *J. Catalysis* **2**, 63 (1963).
8. VOGE, H. H., WAGNER, C. D., AND STEVENSON, D. P., *J. Catalysis* **2**, 58 (1963).
9. SACHTLER, W. M. H., *Rec. Trav. Chim.* **2**, 243 (1963).
10. McCAIN, C. C., GOUGH, G., AND GODIN, G. W., *Nature* **198**, 989 (1963).
11. ERIKEEV, E. KH., ISAEV, O. V., AND MARGOLIS, L. YA., *Kinetika i Kataliz* **1**, 431 (1960).
12. ADAMS, C. R., to be reported at 3rd Intern. Congr. on Catalysis, Amsterdam, 1964.
13. SIXMA, F. L. J., DUYNSTEE, E. F. J., AND HENNEKENS, J. L. J. P., *Rec. Trav. Chim.* **82**, 243 (1963).