The Mechanism of Propylene Oxidation to Acrolein over Bismuth Molybdate, Copper Oxide, and Rhodium Catalysts

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The oxidation of (E)-propene-1-d_1 to acrolein over bismuth molybdate, copper oxide, and rhodium catalysts was studied to determine if the reaction proceeded with (Z)–(E) randomization of the deuterium stereochemistry. Over $Bi_2Mo_2O_9$ and Bi_2MoO_6, (E)-acrolein-3-d_1 : (Z)-acrolein-3-d_1 : acrolein-1-d_1 was 1 : 1 : 1 consistent with a σ-allyl intermediate which rapidly converts between two equivalent forms (*CHD—CH=CH$_2$ ⇆ CHD=CH—*CH$_2$). With copper oxide, (E)-acrolein-3-d_1 : (Z)-acrolein-3-d_1 : acrolein-1-d_1, was 1 : 1 : 1.6. This points to a discrimination isotope effect consistent with a σ-allyl intermediate without interconversion of equivalent forms. Over a Rh/α-Al$_2$O$_3$ catalyst, (E)-acrolein-3-d_1 : (Z)-acrolein-3-d_1 : acrolein-1-d_1 was 1 : 0.93 : 0.89. This is consistent with an allyl intermediate along with a second minor nonallylic pathway which does not equilibrate the terminal carbon atoms. One or both of these processes occurred with some retention of the (E)-deuterium stereochemistry in the acrolein-3-d_1. Over an unsupported Rh catalyst, (E)-acrolein-3-d_1 : (Z)-acrolein-3-d_1 : acrolein-1-d_1 was 1 : 0.68 : 0.85. Only the allylic pathway is evident and the reaction process occurs with incomplete randomization (76 ± 10%) of the (E)-deuterium stereochemistry in the acrolein-3-d_1.

INTRODUCTION

The catalytic oxidation of propene to acrolein has been studied from many perspectives (1). For a number of catalysts, it has been established that the reaction proceeds through a symmetric allylic intermediate which subsequently loses the second hydrogen from either of the equivalent terminal carbon atoms. This has been determined from carbon or deuterium labeling experiments which were reviewed recently (2).

The deuterium results over bismuth molybdate (1a–d, 3), copper oxide (3), and rhodium (4) are noteworthy since they are related to the catalyst systems investigated in this paper. A selection of these results are listed in Table 1. Over the oxide catalysts, an isotope effect was observed in both hydrogen abstraction steps giving rise to nonequal amounts of d_1 and d_2 acroleins from a CH_2CHCD_2 allyl intermediate. However, over supported Rh, the second hydrogen abstraction did not exhibit any

isotope effect and a minor, nonallylic pathway whereby the methyl group was converted to the aldehyde was also observed. The recent work with the bismuth molybdate and rhodium systems has led to the view that oxygen incorporation in the allylic intermediate occurs prior to the loss of the second hydrogen. One possibility is for the π-allyl intermediate to convert to a σ-allyl intermediate perhaps similar to an —O—CH$_2$—CH=CH$_2$ intermediate derived from allyl alcohol (1c).

One aspect of the allylic intermediate has interested us, viz., whether a deuterated propene (PR) labeled stereospecifically (Z) or (E) would retain this geometry in the intermediate through the subsequent oxidation to acrolein (ACR). An isolated allyl radical has a bent C–C–C framework (like PR and ACR) stabilized by its π interaction. In fact the barrier to rotation for (Z)- and (E)-allyl-1-d_1 radicals has recently been determined as 15.7 kcal/mol (5). This barrier could be further raised due to interaction with the catalyst surface. For certain reac-

tion conditions, a σ-allyl intermediate can also convert to acrolein with some stereoselectivity (see below). Consequently, it is conceivable that the overall oxidation of (Z)- or (E)-propene-1-d_1 might occur with some retention of the deuterium stereochemistry relative to the C_3 framework.

A stereolabeled process incorporating σ- and π-allyl intermediates is explored in the reaction network described in Scheme 1 starting with (E)-PR-1-d_1. If complete randomization occurs (for example, $k_E \gg k_{ALA}$ or $k'_{ALA} \gg k_H$) then equal amounts of the E and Z isomers of ACR-3-d_1 will result. If no stereorandomization occurs ($k_E = k'_{ALA} = k_{ALE} = 0$) then the relative amounts of E and Z isomers will be in the ratio of $1:0$. Partial randomization, i.e., unequal (nonzero) amounts of the E and Z products, could also occur. The relative amounts of the ACR-1-d_1 species can also provide useful mechanistic information, for example,

SCHEME 1
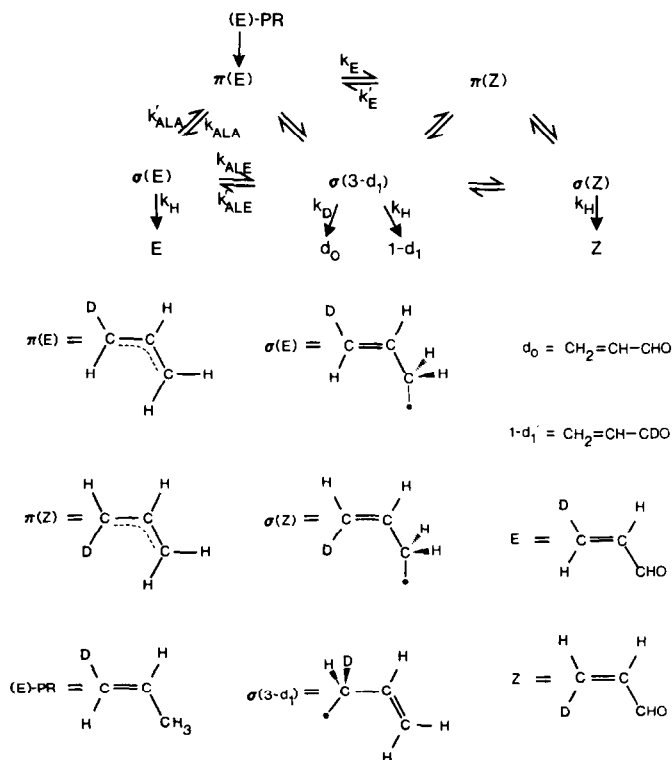
regarding the magnitudes of the above rate constants compared to k_H and k_D or the existence of nonallylic pathways which do not equilibrate the terminal carbon atoms.

The microwave rotational transitions of all the d_1 species of PR and ACR have been assigned (6, 7), so the process of randomization can be followed by their MW spectra. The analysis consists of measuring the relative intensities of suitable transitions for the various species. This provides intensity ratios which can be readily converted into molar ratios. Measurement of the amount of ACR-d_0 would also provide insight on an isotope effect but this was not followed. It was difficult to completely isolate a run with deuterated propene from the preceding stabilization process with normal propene. Moreover, information on d_0/d_1 ratios was initially available from the prior studies as noted above.

METHODS

All catalytic experiments were carried out in a single pass flow reactor described more completely elsewhere (8, 9). Reaction conditions, conversions, and selectivities for typical experiments are listed in Table 2. The gas chromatographic analysis of the feed and effluent has been described (9, 10).

The two bismuth molybdate catalysts were supplied by Dr. Wilbur Swanson, Climax Molybdenum Company, Ann Arbor, Michigan. Pretreatment consisted of air oxidation at 500°C for 1– 2 h.

The 4% Cu_2O/α-Al_2O_3 was prepared from an aqueous solution of $Cu(NO_3)_2$. After impregnation, it was dried in an oven for several days and decomposed to copper oxide in an air flow at 460°C for 15 h. A mixture of propene (10%) and N_2 was passed at 300°C in order to enhance the formation of Cu(I) oxide which is the likely catalytic species. The unsupported copper oxide (Cu_2O, <80 mesh, Aldrich Co.) was also pretreated in this manner.

The 1.5% Rh/α-Al_2O_3 catalyst has been described previously (4, 11). The unsupported Rh metal was prepared from $Rh(NO_3)_2 \cdot 2H_2O$ (12). Surface areas for these catalysts were too low to be measured by conventional hydrogen chemisorption techniques. Pretreatment of each consisted of H_2 reduction for several hours at 300–350°C for several hours following which these systems behaved similarly to the earlier study of the supported Rh catalysts (4, 11).

Following their pretreatment each catalyst was stabilized under reaction conditions with C_3H_6. The labeled PR was then introduced by diverting the oxidant flow through a U-tube containing the PR held as

TABLE 2

Typical Reaction Conditions and Characteristics of the Catalysts

	$Bi_2Mo_2O_9$	Bi_2MoO_6	1.5% Rh/α-Al_2O_3	Rh powder	Cu_2O/α-Al_2O_3	Cu_2O
Surface area (m²/g)	0.16	0.11			0.43	
Catalyst mass (g)	3.8	3.8	2.5	0.1	1.5	0.5
Reactant feed ratio $C_3H_6:O_2:N_2$	2:4:94	2:4:94	1.5:5:93.5	1.5:5:93.5	1:2:97	1.5:1.5:97
Total flow rate (ml/min)	60	60	60	60	60	60
Temperature (°C)	450	450	180	200	250	230
Total conversion of C_3H_6 (%)	8	5	2	0.3	2	2
Selectivity to acrolein (%)	80	85	18	15	45	67
Selectivity to acetone (%)			7	7		

a liquid at a suitable low temperature (*8, 9*). Approximately 1 mmol of labeled compound was fed and the products were collected for analysis. Repassage experiments with (*Z*)-ACR-3-d_1 were conducted similarly under reaction conditions with unlabeled PR in the feed.

The method of analysis of the three d_1-acroleins by microwave spectroscopy has been described previously (*9*). The relative amounts of the (*Z*)- and (*E*)-propene-1-d_1 were similarly determined from the intensity measurements of the same transition for each species. Three transitions were used, viz., the $1_{01}–2_{02}$, $1_{11}–2_{12}$, and $1_{10}–2_{11}$ (*6*). In analyzing the PR-d_1 data, no corrections were made for the small methyl torsion splitting in two (*E*)-PR-d_1 transitions and the factor R needed to convert the MW intensity ratios into a molar ratio was set at 1. The uncertainties in Table 2 contain these considerations and are sufficient to encompass the experimental precision in the measurements. The latter appears to be the limiting factor for the ACR-d_1 system. The somewhat larger uncertainties for ACR-d_1 compared to the earlier study of ACR-d_1 (*9*) result from handling small (micromolar) levels of material particularly over the Rh. An effort was also made to determine the equilibrium (*E*)-ACR-3-d_1/ (*Z*)-ACR-3-d_1 ratio by reanalyzing a partially equilibrated mixture which was left in a glass vessel at room temperature for 6 months. This gave 1.01(1) (*E* = 50.2 ± 1.2%).

The stereolabeled PR-1-d_1 was prepared by reacting methylacetylene and 9-BBN (9-borabicyclo[3.3.1]nonane) in THF followed by CH_3COOD (*13*). Unreacted methylacetylene was removed by reaction with $AgNO_3 \cdot NH_4OH$ and the propene was separated by distillation. This typically produced 75–85% (*E*)-PR-d_1 with the remainder as PR-d_0. The amount of (*Z*)-PR-d_1 was below detection limits (<2%) so no correction for it is needed in estimating the extent of randomization.

The predominantly (*Z*)-ACR-3-d_1 used in

the control experiments was obtained by the oxidative dehydrogenation of (*Z*)-allyl alcohol-3-d_1 to (*Z*)-ACR-3-d_1 as described earlier (*9*). The actual (*E*)-ACR-3-d_1/(*Z*)-ACR-3-d_1 used in repassage runs depended on the batch and was between 0.087 and 0.127. Corrections were made for the (*E*)-ACR-3-d_1 so that the ratio in Table 3 for the recovered material is based on 100% (*Z*)-ACR-3-d_1 in the feed.

RESULTS AND DISCUSSION

Analytical results for the three ACR-d_1 species as well as recovered (unreacted) PR-1-d_1 are listed in Table 3 for 15 experiments. The analysis of the extent of randomization upon passage of (*Z*)-ACR-3-d_1 in a feed containing unlabeled PR is also given for 8 of the experiments. Every effort was made to hold conditions during the repassage of (*Z*)-ACR-3-d_1 closely similar to the related experiment with (*E*)-PR-1-d_1. However, these runs frequently were separated by 4–24 h whereby exact correspondence was precluded.

In discussing these results it is helpful to distinguish between various processes and terms regarding the H and D stereochemistry. (Hereafter, the abbreviations Z, E, and 1-d_1 will refer to the ACR-d_1 species unless noted.)

Symmetrization. Equivalence of end carbons as with the allyl intermediate.

Randomization. Equivalence of H and D as a result of (*Z*)–(*E*) isomerization (i.e., *cis–trans* isomerization).

Product randomization. Equivalence of H and D by (*Z*)–(*E*) isomerization after development of the acrolein double bond. This could occur before desorption or as a consequence of a subsequent readsorption (as experimentally verified). Rapid product randomization will produce *E* = *Z* regardless of the reaction process.

Discrimination isotope effect. It is not possible to see a primary kinetic isotope effect since the slow step is abstraction from the methyl group of (*E*)-Pr-1-d_1. However, a discrimination between H and D is poten-

TABLE 3

Relative Isotopic Distribution from Oxidation of (E)-Propene-1-d_1 or Repassage of (Z)-Acrolein-3-d_1

Run	Catalyst	Temp (°C)	χ^a (%)	Acrolein product[b]			Propylene recovered[b]		Acrolein repassage[c]
				E	Z	$1-d_1$	$Z/(E+Z)$	$(3-d_1)/(E+Z)$	$Z/(E+Z)$
1	$Bi_2Mo_2O_9$	450	8	1.00^d	1.00^e	1.02^f	0.07^d	0.07^d	0.51^d
2	$Bi_2Mo_2O_9$	450	8	1.00	1.00	1.00	0.07	0.07	
3	Bi_2MoO_6	450	5	1.00	1.00	1.02	0.03	0.03	
4	1.5% Rh/α-Al_2O_3	200	8	1.00	0.96	0.92	0.06	0.02	0.59^g
5	1.5% Rh/α-Al_2O_3	180	2	1.00	0.96	0.88	0.02	<0.01	0.68
6	1.5% Rh/α-Al_2O_3	180	5	1.00	0.89	≤0.87	<0.01	<0.01	
7	1.5% Rh/α-Al_2O_3	190	7	1.00	0.92	0.90	0.03	0.03	0.59
8	Rh/unsupported	200	0.3	1.00	0.73	≤0.83	<0.02	<0.02	0.84
9	Rh/unsupported	200	0.5	1.00	0.62	≤0.84	<0.02	<0.02	
10	Rh/unsupported	220	0.9	1.00	0.73	0.88			0.88
11	Rh/unsupported	200	0.2	1.00	0.65	0.84			0.85
12	4% Cu_2O/α-Al_2O_3	250	1.3	1.00	1.04	1.69			0.54
13	4% Cu_2O/α-Al_2O_3	250	1.5	1.00	0.96	1.63			
14	4% Cu_2O/α-Al_2O_3	250	2.7	1.00	1.04	1.47	<0.01	<0.01	
15	Cu_2O/unsupported	230	1.9	1.00	1.04	1.67	<0.02	<0.02	

[a] Total conversion of propylene.

[b] Starting material: 76% (E)-propene-1-d_1, 24% propene-d_0.

[c] Starting material contained predominantly PR-d_0 and (Z)-ACR-3-d_1. The ratios are corrected for the small amounts of (E)-ACR-3-d_1 and apply to 100% (Z)-ACR-3-d_1.

[d] The E-ACR-3d_1 isomer is set at 1.00 and the relative amounts of Z-ACR-3d_1 and ACR-1d_1 (with attached uncertainties) are experimentally determined.

[e] ±0.01 uncertainty for ratios in this column.

[f] ±0.02 uncertainty for ratios in this column.

[g] This ratio was 0.5 for (Z)-ACR-3-d_1 repassage over the α-Al_2O_3 support alone.

tially measurable for the second abstraction process from the ACR-d_0/ACR-d_1 ratio. This ratio was not followed experimentally for the reasons mentioned in the Introduction.

A discrimination between H and D may also be evident indirectly from the relative amounts of the 1-d_1 and $(E + Z)$ species. If k_{ALE} in Scheme 1 is large, then 2×1-$d_1 = (E + Z)$ regardless of k_H and k_D. However, if $k'_{ALA} = k_{ALE} = 0$, then 2×1-$d_1 > (E + Z)$ when $k_H > k_D$. A more extensive analysis of the amounts of the d_0 and d_1 acrolein species expected from Scheme 1 for various rate constant values is explored in Table 4. This table will be used as a basis for interpreting the reaction data.

Bismuth molybdate. The data in Table 3 for the two bismuth molybdate catalysts is clearly explainable by Schemes 1c, d, f, or g (Table 4). Unfortunately, the repassage of (Z)-ACR-3-d_1 also gives essentially complete randomization so this experiment is not helpful in also demonstrating that ACR

reaction randomization occurs. The equivalence of 1-$d_1 : E : Z$ in this work and the observation of a discrimination isotope effect from $d_0 : d_1$ or $d_1 : d_2$ ratios in previous work (Table 1) are mutually consistent with Scheme 1.

Cuprous oxide. The results over copper oxide indicate that 2×1-$d_1 > (E + Z)$. This is only explicable by Scheme 1b (i.e., reaction with stereoretention, followed by product randomization) or Scheme 1e. The relative amounts of 1-$d_1 : E : Z$ can be brought into close agreement with the data in Table 3 for $k_D/k_H \approx 0.25$. This value agrees well with model expectations for this temperature (14). Since control experiments with stereolabeled ACR-3-d_1 undergo nearly complete stereorandomization upon repassage, it is not possible to determine whether the randomization occurs during or after the reaction. In contrast to the bismuth molybdate results, once the σ-allyl species is formed, it does not readily interconvert to another σ-allyl isomer or revert

TABLE 4

Relative Amounts of ACR-d_0, ACR-1-d_1, (E)-ACR-3-d_1, and (Z)-ACR-3-d_1 for the Reaction Network in Scheme 1

Scheme 1	k_E	k'_{ALA}	k_{ALE}	Product acroleins[a]			
				d_0	$1-d_1$	E	Z
a	0	0	0	0.29	0.71	1	0
b[b]	0	0	0	0.29	0.71	0.50	0.50
c	0	0	$\gg k_H$	0.40	1	1	1
d	0	$\gg k_H$	0	0.40	1	1	1
e	$\gg k_{ALA}$	0	0	0.58	1.42	1	1
f	$\gg k_{ALA}$	0	$\gg k_H$	0.40	1	1	1
g	$\gg k_{ALA}$	$\gg k_H$	0	0.40	1	1	1
h[c]	$1.50 k_{ALA}$	0	0	0.80	0.80	1	0.60

[a] Assuming $k_D/k_H = 0.4$ except for Scheme 1h.

[b] Identical to Scheme 1a except that E undergoes complete product randomization after formation.

[c] Product distribution from a steady-state approximation and $k_D = k_H$.

back to the π-allyl species. (It might also be noted that a σ-allyl species is probably not a unique structure for this "terminal" intermediate.)

The results of previous Cu_2O studies (at 350°C) in Table 1 can be compared with the above model. Extrapolation of $k_D/k_H = 0.25$ to the higher reaction temperature (14) predicts a ratio of 14/86 for d_0/d_1 from PR-1-d_1 in good agreement with the observed ratio of 16/84. The same procedure applied to both hydrogen abstraction steps predicts $d_0/d_1 = 29/71$ from PR-3-d_1. Still closer (exact) agreement with the observed value of 35/65 can be obtained by increasing k_D/k_H for the first abstraction to about 0.35–0.40. In summary, the copper oxide results in Tables 1 and 3 appear mutually consistent with Scheme 1b or e.

Rhodium. The results for Rh/α-Al$_2$O$_3$ where 2×1-$d_1 < (E + Z)$ do not fit any schemes in Table 4. The low value of the 1-d_1 isomer is suggestive of a minor pathway where symmetrization of the end carbon atoms does not occur. This was also indicated by other isotopic studies (Table 1) and Scheme 2 was employed to analyze the results (4).

In this scheme, Path A is a symmetrization process such as the allylic mechanism in Scheme 1. Path B is a nonsymmetric or nonallylic mechanism with hydrogen loss and oxygen addition entirely at the methyl carbon such as via a hydroperoxide intermediate. Cant and Hall (4) estimated that $0.74 < y < 0.92$ while $f = 0.49 \pm 0.04$. The latter implies that no isotope effect occurs when the allyl species further oxidizes. The
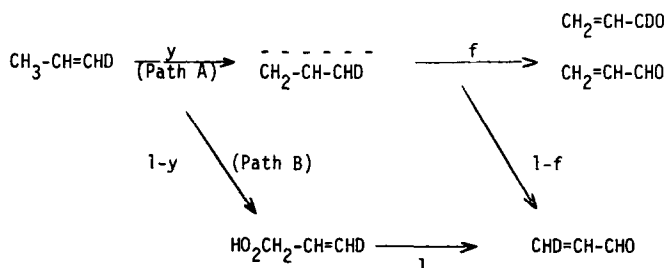
SCHEME 2

Rh/α-Al$_2$O$_3$ data here are also compatible with such a scheme with the added inference that randomization during reaction is incomplete. It does not appear possible to distinguish if the allylic pathway (A) or the nonsymmetric pathway (B) alone is the origin of the nonrandomization. It is also apparent that considerable product randomization occurred by a readsorption process for this system. The α-Al$_2$O$_3$ support is a factor here since repassage of stereolabeled (Z)-ACR-3-d_1 over the support alone led to complete randomization.

These results prompted experiments over unsupported Rh powder in an effort to: (1) significantly alter the relative contributions from paths A and B, (2) alter the relative amounts of the 1-d_1, E, and Z products, (3) minimize the subsequent readsorption–randomization process. The results in Table 3 (runs 8–11) show that these aims were achieved. They indicate that Path B is reduced to a low level since 2 × 1-d_1 = E + Z, within experimental uncertainty. Randomization also decreases including product randomization as demonstrated in separate repassage experiments. In fact a kinetic analysis (cf. Appendix 1) which assumes that Path B is negligible and corrects for the product randomization upon readsorption indicates that 76 ± 10% stereorandomization from the starting material takes place. This implies that E = 24% is obtained by a nonrandomization path while E = Z = 38% is also produced from a reaction randomization pathway.

The data over unsupported rhodium which indicate that 2 × 1-d_1 = (E + Z) along with the data in Table 1 which were used to infer (4) that no isotope effect is observed when the symmetric CD$_2$–CH–

CH$_2$ species further oxidizes to acrolein present one curious possibility to rationalize the data, viz., Scheme 1h. This pathway can approximate the relative amounts of 1-d_1, E, and Z but only if k_H = k_D. It seems surprising that no discrimination isotope effect would occur at the CHD terminus if the σ-allyl intermediate developed the symmetric form illustrated in 1 (Fig. 1). An alternative which preserves the σ-allyl concept would necessitate less symmetric forms such as 2–5. Formation of such intermediates could conceivably occur randomly with little or no apparent isotope effect if catalyst geometry was a factor in formation. If they did not interconvert, they could also proceed to acrolein with no evident discrimination isotope effect. Certainly, it would be worthwhile to further verify the absence of the isotope effect by determining the d_0/d_1 ratio from PR-1-d_1 in future experiments with this system.

Species 2–5 are probably not unique as an explanation for the data. Intermediates containing oxygen might also be possibilities (for example, •OCHD—CH=CH$_2$). In fact, any selection or abstraction of the H versus D on the CHD end of the π-allyl intermediate based primarily on geometric considerations such as proximity to the adsorption site or to the species which promotes abstraction can rationalize the ACR-d_1 data over supported Rh. A more formal analysis of such a thesis is presented in Appendix 2.

Apart from the matter of the isotope effect, it is noteworthy that (E)-PR-1-d_1 can be oxidized over unsupported Rh via a symmetric allyl intermediate with some retention of the (E) stereochemistry in the acrolein. The partial stereorandomization is
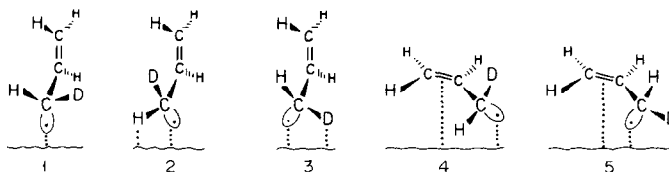

FIGURE 1

curious although not without precedence for catalytic oxidation of alkenes over a metal catalyst (8–10, 15). One explanation (such as in Scheme 1) postulates a competition between the randomization kinetics of the allyl species versus subsequent reactivity to acrolein with retention. An alternative rationale could incorporate two competing reactions at different surface sites (two parallel reactions with and without randomization, respectively). Further experiments exploring the sensitivity of this randomization process to temperature, catalyst properties, and other reaction conditions may shed some light on this question but systematically exploring this for the Rh system appears quite challenging.

SUMMARY

Oxidations of (E)-PR-1-d_1 over bismuth molybdate, copper oxide, and unsupported Rh catalysts all indicated that a symmetrization process occurs as expected for the formation of the π-allyl intermediate. The bismuth molybdate results (both the loss of stereochemistry and $d_1(E + Z)$ ratio) were consistent with conversion of the π-allyl to a σ-allyl intermediate which rapidly interconverts (*CHD—CH=CH$_2$ $\leftrightarrows$ CHD=CH—*CH$_2$). The copper oxide results can be explained similarly except that the σ-allyl intermediates once formed do not interconvert. Oxidation over unsupported Rh suggest that the π-allyl intermediate might convert to a σ-allyl or another intermediate; whatever the detailed fate of the allyl intermediate may be, it further oxidizes with some retention of the original stereochemistry but without a discrimination isotope effect at that stage. Over a supported Rh catalyst a minor nonallylic pathway is also evident.

APPENDIX 1

The Rh/α-Al$_2$O$_3$ data can be analyzed via Scheme 2 to estimate the relative participation of Paths A and B and randomization limits in these paths. This utilizes the isotopic ratios in Table 3 for runs 4, 5, and 7

including the ACR-3-d_1 repassage data and employs the relationships

$$S = \frac{CH_2CHCDO}{CHDCHCHO} = \frac{1-d_1}{E + Z}$$

$$= \frac{0.5\ yf}{y(1 - f) + (1 - y)}$$

$$I = \frac{E}{Z}\ \text{(reaction only)}$$

$$= \frac{y(1 - f)r_a + (1 - y)r_b}{y(1 - f)(1 - r_a) + (1 - y)(1 - r_b)}$$

$$F = \frac{E}{Z}\ \text{(overall)} = \frac{Ir_c + (1 - r_c)}{I(1 - r_c) + r_c},$$

where fraction of acrolein randomization by Path A = $2(1 - r_a)$, that by Path B = $2(1 - r_b)$, and that by readsorption = $2(1 - r_c)$. This implies

$$r_a = \frac{E(\text{Path A})}{(E + Z)(\text{Path A})} \qquad (1 \geq r_a \geq 0.5)$$

and similarly for r_b and r_c. If f is set at 0.5 (4) the equations contain four rate quantities ($y, r_{a,b,c}$) and three experimental ratios (S, F, r_c). From these values of f and S, y can be obtained. From r_c and F, I can be obtained. With I, y, and f fixed, the relationship between r_a and r_b can be examined but not unequivocally separated. It becomes apparent, when experimental uncertainty is considered, that the data are consistent with $r_a = 0.5$–0.7 while r_b varies between 1 and 0.5. The data are very unrestrictive in the range of possible values for r_b since this pathway was quite minor for these runs ($y = 0.95$–0.97).

The same analysis for the unsupported-Rh data shows it to be consistent with $y(\text{ave}) = 1.00 \pm 0.02$ so that Path B has been reduced to a negligible level. The average value of r_a for runs 8, 10, and 11 is 0.62 $\pm$ 0.05 (76 $\pm$ 10% randomization from the starting material). While this is consistent with the rough estimates of r_a over Rh/α-Al$_2$O$_3$, that figure still does not allow much insight to be obtained on whether Path B occurs with randomization or reten-

TABLE 5

Abstraction of Inner versus Outer Hydrogen; Relative Amounts of ACR-d_1 Products from π-Allylic-d_1 Isomers[a]

H(D) loss[b]	d_0[c]	$1-d_1$	E	Z	H(D) loss[b]	d_0[c]	$1-d_1$	E	Z
i(inner)	0	1	1	0	i'(inner)	1	0	0	1
o(outer)	1	0	1	0	o'(outer)	0	1	0	1

[a] See Appendix 2.

[b] Inner loss occurs from the H_2 (or HD) side; outer loss occurs from the H_3 (or H_2D) side.

[c] $k_H = k_D$ apart from geometric effects.

tion over that catalyst. The value of r_a and associated data is still not sufficiently accurate or sensitive enough to Path B to enable a useful estimate of r_b to be made.

APPENDIX 2

A geometrically influenced discrimination between H and D from a π-allylic species will be considered. This could arise if the (E)-allyl-1-d_1 intermediate in Scheme 1 or Table 5 preferentially loses the next H (or D) from the H_2 side (hereafter called the inner side) rather than the H_2D site (hereafter called the outer side) or vice versa. The geometric discrimination might be associated with proximity to the adsorption site or to the species which promotes the abstraction. Apart from this geometric consideration, $k_D/k_H = 1$. The four basic processes that can arise if stereo randomization also occurs in the (E)-π-allyl species before abstraction are listed in Table 5.

The unsupported-Rh data can be reproduced if stereo randomization of the (E)-π-allyl species to (Z)-π-allyl competes with the second abstraction. For example, 1.5(i + o) + (i' + o') results in $d_1 : E : Z = 2.5 : 3 : 2$ close to observed ratios. It is also interesting that the d_1 distribution over Cu_2O in Table 3 can be approximated by 3.1(i + o) followed by E, Z product equilibration in a later readsorption step. How-

ever, such a scheme would also predict $d_0/d_1 \approx 30/70$ starting with (E)-PR-1-d_1 in much poorer agreement with Voge and Adams' results (Table 1) than using Scheme 1b (or 1e). The bismuth molybdate results in Table 3 can also be accommodated by combinations from Table 5 but the results in Table 1 are not reconcilable, especially the data from the CD_2CHCH_2 intermediate. Scheme 1 clearly is superior as a description of the $Bi_xMo_yO_z$ system.

REFERENCES

1. Some recent references on propylene oxidation: (a) Monnier, J. R., and Keulks, G. W., J. Catal. 68, 51 (1981); (b) Krenzke, L. D., and Keulks, G. W., J. Catal. 61, 316 (1980); (c) Burrington, J. D., Kartisek, C., and Grasselli, R. K., J. Catal. 63, 235 (1980); (d) Portefaix, J. L., Figueras, F., and Forissier, M., J. Catal. 63, 307 (1980); (e) Inui, T., Veda, T., and Suehiro, M., J. Catal. 65, 166 (1980); (f) Asao, I., Furakawa, S., Yamazoe, N., and Seiyama, T., J. Catal. 64, 29 (1980).
2. Keulks, G. W., Krenzke, L. D., and Notermann, T. N., in "Advances in Catalysis" (W. G.

Frankenburg, V. I. Komarewsky, and E. K. Rideal, Eds.), Vol. 27, p. 183. Academic Press, New York, 1978.

3. (a) Adams, C. R., and Jennings, T. J., *J. Catal.* **2**, 63 (1963); (b) *ibid* **3**, 549 (1964).

4. Cant, N. W., and Hall, W. K., *J. Catal.* **22**, 310 (1971).

5. Korth, H.-G., Trill, H., and Sustmann, R., *J. Amer. Chem. Soc.* **103**, 4483 (1981).

6. Lide, Jr., D. R., and Mann, D. E., *J. Chem. Phys.* **35**, 1374 (1961).

7. Cherniak, E. A., and Costain, C. C., *J. Chem. Phys.* **45**, 104 (1966).

8. Egashira, M., Kuczkowski, R. L., and Cant, N. W., *J. Catal.* **65**, 297 (1980).

9. Imachi, M., Cant, N. W., and Kuczkowski, R. L., *J. Catal.* **75**, 404 (1982).

10. Imachi, M., Egashira, M., Kuczkowski, R. L., and Cant, N. W., *J. Catal.* **70**, 177 (1981).

11. Cant, N. W., and Hall, W. K., *J. Catal.* **16**, 220 (1971).

12. Sinfelt, J. H., and Yates, D. J. C., *J. Catal.* **8**, 82 (1967).

13. Brown, H. C., Knights, E. F., and Scouten, C. G., *J. Amer. Chem. Soc.* **96**, 7765 (1974).

14. Melander, L., *in* "Isotope Effects on Reaction Rates," p. 22. Ronald Press, New York, 1960.

15. Cant, N. W., and Hall, W. K., *J. Catal.* **52**, 81 (1978).