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The Mechanism of the Oxidation of Propene to Acrolein over Copper Oxide

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The oxidation of stereo-labeled propene to acrolein over copper oxide was studied to obtain information about the nature of the intermediates involved in the second hydrogen abstraction and oxygen incorporation process. Experiments with (*E*)—CHD═CHCH$_3$ and (*Z*)—CHD═CHCH$_3$ gave deuterated acrolein product ratios which were independent of the stereochemistry of the starting material. The amounts of (*E*)-acrolein-3-d_1, (*Z*)-acrolein-3-d_1, and acrolein-1-d_1 were in the ratio of 1 : 1 : 1.6 which are consistent with irreversible conversion of a π-allyl to a σ-allyl intermediate. They exclude a geometric discrimination effect in the second H abstraction step. The reaction of (*E*)-CHD═CDCH$_3$ was also consistent with irreversible formation of a σ-allyl species and gave a discrimination isotope effect of 0.37 ± 0.06 for the second H abstraction. The results from the oxidative dehydrogenation of D- and ^{18}O-labeled allyl alcohol show no end-to-end deuterium scrambling and partial loss of ^{18}O in the acrolein. This suggests that a σ-allyl species bonded to the surface through oxygen does not equilibriate between the end carbon atoms before desorbing to acrolein. The differences in behavior of the σ-allyl intermediates over copper oxide and molybdate catalysts are discussed.

INTRODUCTION

Bismuth molybdate and copper oxide were early prototype catalysts for the oxidation of propene to acrolein (*1*). Although they have been superceded in commercial applications by newer catalysts, they have continued to draw attention for mechanistic studies. Considerable insight has been garnered on the conversion process over bismuth molybdate catalysts (*2*) while the picture over copper oxide has been developed in less detail (see Ref. (*3*) for some recent studies). It has been established that a symmetric allyl intermediate is a precursor to acrolein in both catalyst systems.

We recently reported (*4*) on the oxidation of (*E*)-propene-1-d_1 (hereafter E-PR) to acrolein over these catalysts and found some unexpected differences using isotopic tracers. The amounts of (*E*)-acrolein-3-d_1 (E-ACR or ACR-3-d_1), (*Z*)-acrolein-3-d_1 (Z-ACR), and acrolein-1-d_1 (ACR-1-d_1) were 1 : 1 : 1 over bismuth molybdate but 1 : 1 : 1.6 over copper oxide. The amounts of ACR-d_0 were not determined because the main interest was to follow the E and Z stereochemistry in the acrolein and because of concerns that some of the ACR-d_0 might arise from the preceding stabilization process with normal propene.

These results were consistent with a mechanism involving conversion on a π-allyl intermediate to a σ-allyl intermediate followed by production of acrolein (Scheme 1). In the case of bismuth molybdate, the σ-allyl intermediate must rapidly convert between the three σ-allyl isomers (k'_{ALA} or $k_{\mathrm{ALE}} \gg k_{\mathrm{H}}$). Consequently, a deuterium discrimination isotope effect in the second H(D) abstraction involves C—D bond breakage in competition with the three terminal C—H bonds resulting in E-ACR = Z-ACR = ACR-1-d_1 > ACR-d_0. In the case of copper oxide, the three σ-allyl species do not interconvert (for example $k_{\mathrm{E}} \gg$

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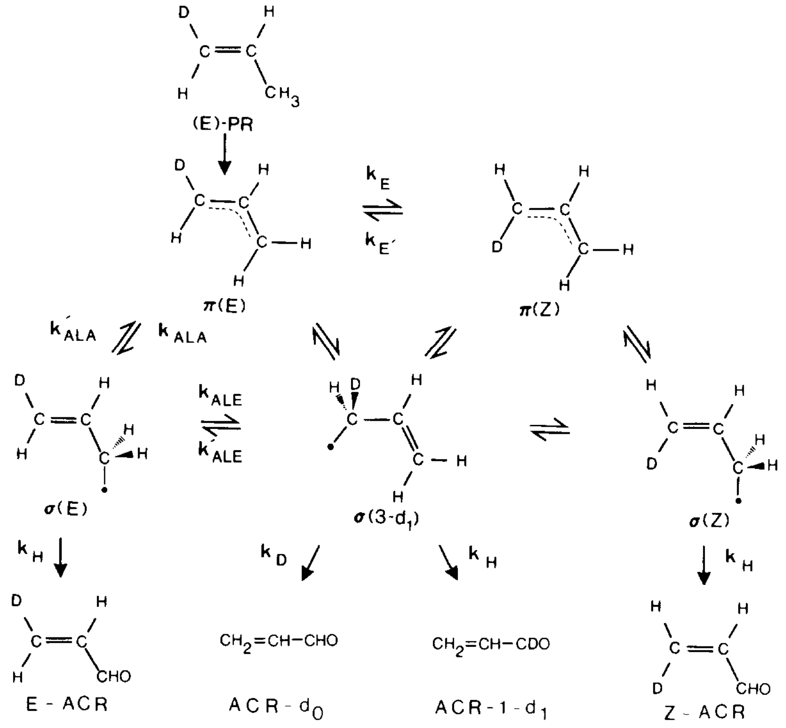


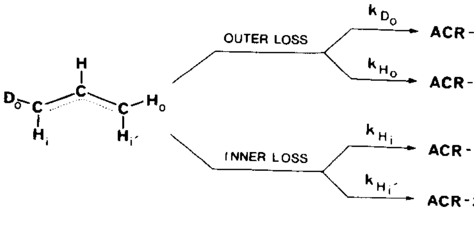
SCHEME 1

0, $k'_{ALA} = k_{ALA} = 0$). Therefore the C—D bond breakage is in competition only with the vicinal C—H terminal bond in $\sigma(3-d_1)$ requiring that (E-ACR + Z-ACR) = $(ACR-d_0 + ACR-1-d_1)$ or alternatively E-ACR = Z-ACR < $ACR-1-d_1$ > $ACR-d_0$ provided that $k_H > k_D$.

A second mechanism which could account for the copper oxide data was also discussed (*4*). This considered a geometric model with a preferred abstraction of the inner H_i or H'_i versus outer H_o or D_o from a π-allyl species obtained from E-PR (Scheme 2). E, Z equilibration in the product acrolein must also occur in a later adsorption step.

If abstraction of the inner hydrogens is preferred over the outer ones (perhaps due to proximity to the absorption site or to the species which promotes abstraction), the amount of ACR-1-d_1 relative to the ACR-3-d_1 would increase compared to reactions over bismuth molybdate. For example, in the limit where only inner hydrogens are abstracted and the ACR-3-d_1 equilibrates between the E and Z isomers, the ratio would be 1 : 1 : 2 for E-ACR:Z-ACR:ACR-1-d_1. This mechanism was less attractive since it did not agree as well with the amounts of ACR-d_0 and d_1 obtained by Voge and Adams with $CH_3CH = CHD$ (*1*).

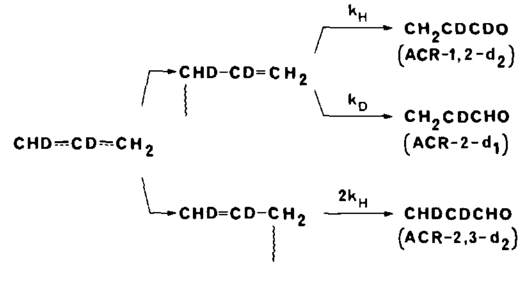
It seemed worthwhile to extend the copper oxide results with data from several additional isotopic species. This would serve to discriminate more definitively between Schemes 1 and 2 and to further confirm and elucidate the mechanistic differences between the bismuth molybdate and copper



SCHEME 2

oxide catalysts. Two experiments using deuterium tracers were conceived. First, Scheme 1 would predict that the oxidation of (*Z*)-propene-1-d_1 (Z-PR) would lead to E-ACR = Z-ACR < ACR-1-d_1, i.e., the same results as obtained previously with E-PR while Scheme 2 gives E-ACR = Z-ACR > ACR-1-d_1. Second, the investigation of CH_3—CD=CHD would enable determination of the four possible acrolein products in a single experiment permitting an estimate of the deuterium isotope effect in the second H/D abstraction step without any interference from products arising from CH_3—CH=CH_2 used during the catalyst stabilization stage. If Scheme 1 is correct, the product yields should be (E-ACR-2,3-d_2 + Z-ACR-2,3-d_2) = (ACR-2-d_1 + ACR-1,2-d_2) (see Scheme 1a). However, this ratio of products would only be true for Scheme 2 if no discrimination isotope effect occurs in the H,D abstraction from CH_2—CD—CHD.

In addition to these two isotopic experiments, some exploratory work dealing with the oxidation of deuterium-labeled and ^{18}O-labeled allyl alcohol were also carried out. It was hoped that this might provide some additional insights on the suspected nature of the intermediates leading to acrolein over a copper oxide catalyst.



SCHEME 1a

METHODS

The basic experimental procedure including flow reactor, supported and unsupported copper oxide catalyst, preconditioning procedure, and analysis of catalyst activity have been described previously (*4*). Typical reaction conditions in the present study are given in Table 1. In runs 1–7 (Table 2), the stabilization of the catalyst prior to injection of the isotopic species employed either normal propene or allyl alcohol. For runs 8 and 9, CHD=CH—CH_2OH was used to stabilize the working catalyst prior to injection of the allyl alcohol-^{18}O so that no unlabeled acrolein from the stabilization treatment could contaminate the ^{18}O results. Runs 10 and 11 which check for loss of ^{18}O in acrolein were similar to Runs 8 and 9 substituting acrolein for allyl alcohol. Proton NMR were obtained with a Bruker AM-300 spectrometer. Microwave spectra were measured with an HP 8640 spectrometer.

The sample of (*E*)—CH_3—CH=CHD was prepared by reacting methylacetylene and 9-BBN in THF followed by CH_3COOD (*5*). This gave approximately 80% E-PR-d_1

TABLE 1

Typical Reaction Conditions for Oxidations over Copper Oxide Catalysts

Reactant	(*Z*)—CHD=CH—CH_3	(*E*)—CHD=CD—CH_3	(Z)—CHD=CH—CH_2OH	CH_2=CH—$CH_2^{18}OH$
Catalyst	4% Cu_2O/Al_2O_3	4% Cu_2O/Al_2O_3	Cu_2O	4% Cu_2O/Al_2O_3
Feed ratio $C_3:O_2:N_2$	5:2:93	5:2:93	1.6:1.3:97	1.3:0.7:98
Total flow rate (ml/min)	55	55	60	60
Temp. (°C)	237–240	240	290	290
Total conv. (%)	1–2	1–2	60–65	ND
Selectivity to acrolein (%)	37–64	47–66	96	ND

TABLE 2

Relative Isotopic Distribution in Acrolein from Labeled Propylene, Allyl Alcohol, or Acrolein over Copper Oxide

Run	Reactant (%Enrichment)	Acrolein product			
		(*Z*)—CHD=CH—CHO	(*E*)—CHD=CH—CHO	CH_2=CH—CDO	
1	(*Z*)—CHD=CH—CH_3(>99)	1	0.98(4)	1.62(6)	
2	(*Z*)—CHD=CH—CH_3(>99)	1	0.92(3)	1.56(3)	
3	(*E*)—CHD=CH—CH_3(>99)	1	0.96(3)	1.66(5)	
		(*Z*)—CHD=CD—CHO	(*E*)—CHD=CD—CHO	CH_2=CD—CDO	CH_2=CD—CHO
4	(*E*)—CHD=CD—CH_3(95)[a]	1	1.09(13)	1.60(13)	0.59(13)
5	(*E*)—CHD=CD—CH_3(95)	1	1.00(7)	1.52(15)	0.55(5)
		(*Z*)—CHD=CH—CHO	(*E*)—CHD=CH—CHO	CH_2=CH—CDO	
6	(*Z*)—CHD=CH—CH_2OH(85)[b]	1	0.82(2)[c]	0.00(1)	
7	(*Z*)—CHD=CH—CH_2OH(85)[b]	1	0.86(2)[c]	0.00(1)	
		CH_2=CH—$CH^{16}O$	CH_2=CH—$CH^{18}O$		
8	CH_2=CH—$CH_2^{18}OH$(40)	1	0.12(2)		
9	CH_2=CH—$CH_2^{18}OH$(40)	1	0.17(2)		
10	CH_2=CH—$CH^{18}O$(55)	1	0.59(5)		
11	CH_2=CH—$CH^{18}O$(55)	1	0.80(6)		

[a] 2%(*E*)—CHD=CH—CH_3, 3% CH_2=CD—CH_3. The product ratios were corrected to 100% (*E*)—CHD=CD—CH_3.

[b] 15% (*E*)—CHD=CH—CH_2OH.

[c] The product ratio is not adjusted for the (*E*) isomer in the feed.

with the remainder as PR-d_0. The amount of Z-PR-d_1 was below detection limits (<1%) so no correction for this species is needed in analyzing the acrolein products. The (*Z*)—CH_3—CH=CHD was prepared similarly using $CH_3C{\equiv}CD$ (*6*) and again no trace of the opposite E stereoisomer was observed. Microwave spectroscopy was employed for the deuterium analyses (*4*).

The sample of (*E*)—CH_3—CD=CHD was prepared from CH_3—C≡CH and disiamylborane-d_1 (*7*) followed by a workup employing CH_3COOD (*5*). A MW analysis (*4*) indicated that it contained 95% (*E*)—CH_3—CD=CHD, 2% (*E*)—CH_3—CH=CHD, and 3% CH_3—CD=CH_2.

The (*Z*)—CHD=CH—CH_2OH was prepared by reduction of propargyl alcohol with $LiAlH_4$ followed by addition of D_2O as described in a previous report (*8*). Analysis by NMR and MW spectroscopy (*8*) indicated that it contained 85% (*Z*)—CHD=CH—CH_2OH and 15% of the E isomer.

The sample of CH_2=CH—$CH^{18}O$ was prepared by hydrolysis of 20 mmol of acrolein dimethyl acetal with an approximately 1 : 1 mixture of $H_2^{18}O/H_2^{16}O$ using a modified literature procedure (*2b*, *9*). The reaction was monitored by NMR. After extraction with ether, the acrolein was separated by trap-to-trap distillation on a high-vacuum line. Analysis by MW spectroscopy gave 54.6% acrolein-^{18}O and 43.4% acrolein-^{16}O. Allyl alcohol-^{18}O was prepared by addition of the ether layer to $NaBH_4$ (30 mmol) in ether (50 ml); the reaction was then monitored by NMR. After 5 h of reflux, 10% HCl was added until no H_2 was evolved. Trap-to-trap distillation produced a mixture of MeOH and allyl alcohol which was used without further purification since the CH_3OH did not affect the catalysis. GC–MS indicated that the allyl alcohol was 40% ^{18}O-enriched.

Microwave spectroscopy was used to determine the relative amounts of the isotopic acrolein products. Three sets of rotational transitions were compared and the peak intensities were converted into molar ratios following a procedure described elsewhere (*8*). This was not a sufficiently large set of transitions to obtain very high precision with a small sample (~20 μmol of product) containing four isotopic species. Nevertheless the precision in the isotopic ratios in Table 2 is sufficient to provide unambiguous insights on reaction processes.

RESULTS AND DISCUSSION

The results in Table 2 for experiments with Z-PR (Runs 1,2) and a cross-check with E-PR (Run 3) show that the amount of Z-ACR:E-ACR:ACR-1-d_1 are 1.00 : 0.95(5) : 1.61(6) and independent of the stereochemistry of the starting material. Negligible randomization was found in recovered starting material ($\leq 2\%$) (*4*). As discussed in the Introduction, this is expected for Scheme 1 if $k_{\mathrm{ALE}} = k_{\mathrm{ALA'}} = 0$ which implies no interconversion of the σ-allyl species. These results are not compatible with a geometric discrimination effect (Scheme 2). The indication of a small preference for Z-ACR over E-ACR is not established unambiguously considering the small set of MW transitions available for analysis and possible systematic errors from nearby transitions, baseline determination and vibrational partition function corrections. These results also cannot establish whether the extensive E-Z randomization in the acrolein occurs during the formation of the allyl species ($k_{\mathrm{E}} \neq 0$ for example) or after the product is formed. In a control experiment with Z-ACR, at least 92% of the acrolein stereo-randomized when passed over the catalyst under reaction conditions (*4*).

The experiments with (E)—CHD=CD—CH_3 (Runs 4, 5) indicate that (E-ACR-2,3-d_2 + Z-ACR-2,3-d_2) : (ACR-1,2-d_2 + ACR-2-d_1) are in the ratio of 1.00(7) : 1.04(13). This implies that half of the acrolein (within the experimental uncertainty) was derived from each of the two σ-allyl intermediates in Scheme 1a. This is consistent with Scheme 1a (and Scheme 1) if the σ-allyl species do not interconvert and if there is no isotope effect in the formation of the σ-allyl species. A discrimination isotope effect of 0.37 ± 0.06 can be deduced from the ACR-1,2-d_2 and ACR-2-d_1 products. This is a reasonable value based on expectations for the reaction temperature (*10*).

It is reasonable to suppose that —O—CH_2—CH=CH_2 or —O—$\dot{C}$H—CH=CH_2 (or even both) are the σ-allyl precursor(s) to the desorbed acrolein since it is difficult to unambiguously establish whether the oxygen is added before, after, or simultaneous to the loss of the H from the π-allyl species (see Ref. (*3c*) for evidence for a σ—$CH_2CH{=}CH_2$ species). The results with the deuterated propenes would then suggest that the oxidative dehydrogenation of CHD=CH—CH_2OH might lead exclusively to CHD=CH—CHO. The results from Runs 6 and 7 over unsupported copper oxide are consistent with this expectation and furthermore show nearly complete stereorandomization (55% Z-ACR, 45% E-ACR) about the double bond. The amounts of CH_2=CH—CDO were below 1%. In the absence of additional control experiments, it is unclear whether the stereorandomization occurs in the original allyl alcohol, in an adsorbed intermediate or during a readsorption of the acrolein product. A similar loss of stereochemistry was observed in the oxidation of allyl alcohol over Ag for low-feed O_2 conditions (*8*).

An important experiment involving C_3H_6 and $^{18}O_2$ over Cu_2O had previously reported that the ^{18}O label was found entirely in the acrolein (*3d*). The conversion of allyl alcohol-^{18}O should also produce predominantly acrolein-^{18}O if the two reactions have common σ-allyl intermediates. However, the observed behavior was more complex. The results of Runs 8 and 9 show that 2/3 of the label in the allyl alcohol-^{18}O is lost in the acrolein. When acrolein-^{18}O is passed over the catalyst under reaction conditions (Runs 10, 11), approximately 1/3 of the label is exchanged. This indicates that up to approximately 50% of the label in the allyl alcohol-^{18}O was lost prior to appearance of the acrolein. It is possible that some of this occurs due to exchange or oxidation of the allyl alcohol over the alumina support but control experiments were precluded due to the unavailability of sufficient allyl alcohol-^{18}O to explore such possibilities. In summary, the allyl alcohol-^{18}O results are consistent with a considerable amount (at least 50%) of the oxygen in the allyl alcohol tracking to the acrolein followed by some additional loss of the ^{18}O label in a subsequent acrolein readsorption–desorption process. Since the allyl alcohol-^{18}O and C_3H_6-$^{18}O_2$ results were conducted over supported and unsupported catalysts, respectively, some ambiguity exists as to whether the apparent quantitative difference in retention of the ^{18}O label for the two systems is mechanistically significant. At this point it is preferable to emphasize that the two system behave qualitatively similarly (i.e., considerable retention of the ^{18}O label occurs) as expected for processes with common reaction intermediates and to withhold judgment on the quantitative differences until their origin and significance is more clearly established.

The results from both the ^{18}O- and D-labeled allyl alcohol imply that a σ-allyl species containing oxygen on copper oxide is not prone to randomize the end carbon atoms, i.e., does not equilibrate between equivalent σ-allyl forms. This is parallel to the behavior of the σ-allyl species formed from propylene. This can be contrasted to the results over bismuth molybdate and molybdenum oxide where a deuterium-labeled allyl alcohol precursor gave considerable deuterium labeling at both terminal carbon atoms in the acrolein and ^{18}O-allyl alcohol exchanged oxygen extensively with the catalyst at acrolein forming sites (*2b, 2d*). Of course this behavior is also consistent with the facile interconversion of equivalent σ-allyl species formed from propylene over these catalysts.

This study clearly delineates that the surface allyl intermediates which occur during the oxidation of propene and allyl alcohol over copper oxide and bismuth molybdate behave differently in the latter stages of the process contrary to some earlier views on these catalysts (*1a, 1b*). The proposed irreversible transformation of the π-allyl to σ-allyl species over copper oxide is similar to the model describing the oxidation and ammoxidation process over antimonate catalysts (*2e, 11*). In the case of the antimonate systems, the $\pi \rightarrow \sigma$ conversion is also irreversible while for molybdate catalysts the $\pi \leftrightarrow \sigma$ interconversion is facile leading to equilibration between the σ-allyl species in Scheme 1. The difference between the molybdate and antimonate catalysts has been explained (*2e*) as intrinsic to the terminal unsaturated Mo=O groups in the one system in contrast to the bridging Sb—O—Sb linkages in the other. Thus conversion of a π-allyl to σ-antimonate intermediate ($Sb—O—CH_2—CH=CH_2$) is less reversible than the corresponding σ-molybdate formation which represents insertion into bridging vs unsaturated metal–oxygen bonds. The presence or absence of adsorbed surface oxygen apparently does not affect this interconversion as evidenced by studies of the systems both in the presence and absence of feed O_2 (*2b–e*).

In the copper oxide system the low oxygen atom ratio in the nominal Cu_2O catalyst and the unlikelihood of substantial quantities of unsaturated Cu=O surface sites makes a mechanistic process similar to the molybdate system unattractive. Bridging Cu—O—Cu linkages are a more plausible reason for the similarity in behavior of the σ-allyl species on copper oxide and antimonate catalysts in contrast to molybdate catalysts. However, the C_3H_6-$^{18}O_2$ study mentioned above (*3d*) suggests that an adsorbed oxygen species as opposed to surface lattice oxygen is incorporated into the acrolein. In this proposal, the lattice oxygen acts as the initial H extraction center while an adsorbed oxygen species (O_2^- or O^- were proposed) is incorporated into the allyl intermediate. This proposal is easily compatible with the behavior observed in the present study. In summary, regardless of the origins of the oxygen in a σ-allyl precursor to acrolein, the present work argues that over copper oxide catalysts any σ-allyl intermediates whether or not containing oxygen do not undergo $\sigma \leftrightarrow \sigma'$ or $\sigma \leftrightarrow \pi$ interconversion under reaction conditions.

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