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The Stereochemistry of the Oxidative Dehydrogenation of Allyl Alcohol-3-d_1 over a Silver Catalyst

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The stereochemistry of the oxidative dehydrogenation of (*Z*)-allyl alcohol-3-d_1 to acrolein over a silver catalyst has been studied using microwave spectroscopy for analyses. With oxygen present randomization was less than 16% over the temperature range 160–290°C. In the absence of oxygen acrolein was still produced by dehydrogenation but randomization rose to 60–80% and some propionaldehyde-d_1 was observed. Under both conditions repassage of stereolabeled acrolein along with unlabeled allyl alcohol led to similar amounts of randomization to the above. The data indicate that the reaction of allyl alcohol occurs with retention of alkene stereochemistry while a repeated readsorption process leads to randomization in the acrolein. It would appear likely that the primary interaction of acrolein and allyl alcohol with the reduced silver is via the oxygen atom of each. Thus the chemistry does not involve the formation of π-allyl intermediates as observed with oxide catalysts.

INTRODUCTION

The heterogeneous oxidation of allyl alcohol to acrolein in the presence of air is not a process in wide use although there are numerous references to the reaction (*1*). Various catalysts produce acrolein including Ag (*2, 3*), Cu (*4–7*), Pt (*8–10*), Pd (*7, 8, 11*), as well as metal oxides (*12–15*). We were motivated to investigate the mechanism of this oxidation over silver in order to prepare stereolabeled acrolein-d_1 which was needed for other experiments. There are no literature reports on this material and standard routes to acrolein including the widely used catalytic oxidation of propylene are not suitable for its preparation (*16*). We report herein the results from oxidation of (*Z*)-allyl alcohol-3-d_1 over Ag powder in the presence and absence of feed oxygen. Several interesting contrasts have been found including high retention of stereochemistry in the presence of O_2 but high randomization in its absence.

EXPERIMENTAL

All catalytic experiments were carried out in a single pass flow reactor with temperature controlled to about 1°C. Two grams of silver sponge was held in a tubular (10.5-mm-i.d.) pyrex reactor. The silver sponge was used previously in studies of ethylene and propylene epoxidation and its preparation and characterization are described in those reports (*17–19*). The catalyst was reduced with hydrogen at 320°C for several hours prior to each run. It was stabilized by oxidation of allyl alcohol for 2–4 hr at the desired temperature followed by passage of deuterated allyl alcohol or acrolein for 5 to 10 min.

The carrier gas was nitrogen (prepurified, 99.95%) in all experiments and the total flow rate was maintained at 60 cm^3 min^{-1}. Normal and labeled allyl alcohol were added to the feed by passing the nitrogen over several milliliters of the alcohol in a U trap at room temperature. Its concentration

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in the feed was 1% on the average. When necessary, oxygen (extra dry, 99.6%) was added at a concentration of 1.5%. For repassage experiments under reaction conditions, a small amount of stereolabeled acrolein was held in a trap at −23°C and the flow was diverted over it. This resulted in a concentration of about 0.3% in the total feed.

Unlabeled allyl alcohol was obtained from Mallinckrodt Co. with a purity determined as ~99%. Stereolabeled (*Z*)-allyl alcohol-3-d_1 (hereafter, *cis*-ALA-3-d_1) was prepared by the reduction of propargyl alcohol with $LiAlH_4$ in ether followed by the addition of D_2O at low temperature (*20*). Solvent was removed by distillation while unreacted propargyl alcohol and byproducts were removed by GC separation using a Carbowax 1000 column at 90°C. This resulted in 76% *cis*-ALA-3-d_1 and 24% normal ALA. No other deuterated species could be detected by microwave spectroscopy. This gave a limit of 0.03 for the *trans*-3-d_1/*cis*-3-d_1 ratio in the starting material. The microwave assignment of the normal ALA is known (*21*) and the assignment for ALA-3-d_1 will be reported elsewhere (*16*).

The products were sampled for GC analysis or collected at −160°C for spectroscopic analysis. The latter samples were distilled through −45 and −96°C traps in order to separate and concentrate the acrolein and allyl alcohol.

The *cis*-3-d_1/*trans*-3-d_1 ratio in the acrolein was determined by measurement of the relative intensities of the same microwave transition for the two species. This analytical technique has been discussed previously (*18, 22*) and the MW assignment for these isotopic species was also available (*23, 24*). Three pairs of rotational transitions were used to obtain the intensity ratio. They were the 4_{04}–3_{03}, 4_{14}–3_{13}, and 4_{13}–3_{12} transitions. The factor *R* needed to convert the microwave intensity ratio into a molar ratio was 1.025, 1.020, and 1.034, respectively. The average deviation of the percentage (*Z*)-acrolein-3-d_1 (hereafter, *cis*-ACR-3-d_1) for the three transitions was less than ±0.5%. The absolute accuracy however is estimated to be ±2%. This is obtained by considering the experimental precision as well as possible systematic errors from uncertainties in the dipole moments or the assumption that the ratio of vibrational partition functions is 1. These sources of error have also been discussed previously (*18, 22*).

In some experiments *cis*-ACR-3-d_1 was added to the feed in order to determine if it led to propionaldehyde-d_1. The isotopic enrichment in the recovered propionaldehyde was determined by MW spectroscopy (*25*). This necessitated assignment of the rotational transitions of CH_2DCH_2CHO which will be reported separately (*16*). Authentic samples of CH_2DCH_2CHO were employed. They were obtained by the catalytic isomerization of $CHD{=}CHCH_2OH$ over γ-Al_2O_3 at 325°C (*13*). (On this catalyst, selectivity to propionaldehyde was above 90% and no acrolein was formed.)

A Varian-920 gas chromatograph was employed to analyze the reactant and product gases using three columns: 10% Carbowax 1000 on Chromosorb WHP at 60°C for analysis of acrolein, propionaldehyde, and allyl alcohol, Porapack Q at 75°C for CO_2, and molecular sieve 5A for O_2 and N_2. Attempts were made to detect by GC if H_2, glycidol, or propanol were present in the effluent. Any H_2 or glycidol in the mixture was below detection limits of 0.2% and 0.001%, respectively. Propanol was present in about 0.5%, an amount similar to that in the allyl alcohol starting material.

In several experiments, stereolabeled *cis*-ACR-3-d_1 was passed over the catalyst to evaluate the possibility of an adsorption–randomization process. This was done under reaction conditions by adding the acrolein to a feed containing unlabeled ALA. The labeled acrolein was 92.6% *cis*-3-d_1 and 7.4% *trans*-3-d_1. It was prepared by the oxidation of *cis*-ALA-3-d_1 over Ag (with O_2) at 290°C and analyzed by microwave spectroscopy. It was also found that stereolabeled acrolein randomized slowly when

stored for several days at room temperature. This necessitated storage of labeled acrolein in liquid N_2 until it could be analyzed by MW spectroscopy or used in a repassage experiment.

RESULTS

Selectivity (S_{ACR}), total conversion (χ_T), and randomization at different temperatures are summarized in Tables 1 and 2 for reactions in the presence and absence of O_2, respectively. Unlike other oxidation reactions studied over this catalyst (*17–19*), the results were not closely reproducible from run to run. This probably results from the reaction being sensitive to the preconditioning procedure or to small differences in the feed concentrations. However, it did not seem worthwhile to pursue this matter in further detail since overall reactivity patterns were clear enough.

For reactions in the presence of O_2, high conversions and selectivities to ACR were found at temperatures ≥210°C. CO_2 and H_2O were also produced but no other partial oxidation products were detected. In the absence of O_2, the conversion dropped markedly although it was still appreciable at 250–300°C. The selectivity to acrolein at these temperatures was nevertheless quite high. Propionaldehyde, which is an isomer of ALA, was also observed but CO_2 or H_2O was absent. Mass balance required some hydrogen production but the quantities likely to be produced were below GC detection limits.

The amount of stereorandomization in the product ACR-3-d_1 was clearly low in the presence of O_2 (percentage randomization ≤16%) while high in the absence of O_2 (60% ≤ % rand ≤ 83%). There was no clear trend in the percentage randomization with temperature although there were some hints that lower temperatures decreased the amount of randomization in Table 1 but increased it in Table 2. More extensive data are needed to unambiguously establish such patterns. There does appear to be a correlation in Table 2 between randomization and selectivity considering both the oxidation and repassage experiments. The lower randomizations (60–70%) are associated with high selectivities ≥93% while higher randomization (76–83%) occurred with selectivities in the range 74–82%.

The amount of stereorandomization when stereolabeled ACR-3-d_1 was repassed over the catalyst under reaction conditions

TABLE 1

Catalytic Dehydrogenation of Allyl Alcohol to Acrolein in the Presence of Oxygen

Run	Temperature (°C)	Reaction of normal allyl alcohol		Reaction of *cis*-allyl alcohol-3-d_1			
		χ_T(%)	S_{ACR}(%)[a]	χ_T(%)	S_{ACR}(%)	*cis*-ACR-3-d_1(%)	Rand.(%)
1	160	15.9	99.4	16.0	99.5	96.3	7.4
2	210	96.6	98.8	91.5	99.3	92.3	15.4
3	250	90.7	99.5	96.1	99.3	94.3	11.4
4	290	100	96.8	100	96.3	94.9	10.2
5	290	100	95.2	100	92.1	92.2	15.6
				Repassage of *cis*-acrolein-3-d_1[b]			
6	200	48.8	99.9	—	—	91.5	2.6[c]
7	290	100	89.4			86.0	15.5

[a] Other products are CO_2 and water.
[b] 92.6% *cis*-ACR-3-d_1 and 7.4% *trans*-ACR-3-d_1 added to a feed containing ALA-d_0.
[c] Based on 100% *cis*-ACR-3-d_1 starting material.

TABLE 2

Catalytic Dehydrogenation of Allyl Alcohol to Acrolein in the Absence of Oxygen

Run	Temperature (°C)	Reaction of normal allyl alcohol		Reaction of *cis*-allyl alcohol-3-d_1			
		χ_T(%)	S_{ACR}(%)[a]	χ_T(%)	S_{ACR}(%)	*cis*-ACR-3-d_1(%)	Rand.(%)
1	200	6.2	98.9	5.4	100	65.6	68.9
2	200	7.2	80.8	9.1	87.0	59.7	80.6
3	250	26.4	73.9	19.4	77.8	61.9	76.2
4	300	28.6	93.0	24.0	96.1	69.8	60.4
				Repassage of *cis*-acrolein-3-d_1[b]			
5[c]	200	6.3	99.5	—	—	64.5	66.0[d]
6	200	9.7	81.4	—	—	58.7	79.7
7	200	10.2	75.7	—	—	57.4	82.6
8	300	48.5	96.3	—	—	64.8	65.3
9	300	27.5	93.8	—	—	65.0	64.8

[a] Other products are propionaldehyde and presumably H_2.

[b] See footnote *b*, Table 1.

[c] Run 5 was followed by run 1 so that the stereochemistry could be compared for nearly identical reaction conditions.

[d] See footnote *c* in Table 1.

was generally similar to the amount observed when ALA-3-d_1 was oxidized. One set of stereoexperiments (Runs 5 and 1, Table 2) was carried out seriatim in order to match the reaction conditions as closely as possible for the oxidation of the labeled ALA and the repassage of labeled ACR in the presence of unlabeled ALA. The amount of randomization in the recovered ACR agreed closely for the two cases.

The MW spectrum indicated that there was negligible *cis/trans* isomerization in unreacted ALA-3-d_1. There was no evidence in the MW spectrum for any CH_2=CHCDO in the product gases for any runs indicating that it was below 1% compared to CHD=CHCHO. However, when CHD=CHCHO was repassed over the catalyst under reaction conditions, an appreciable amount of the recovered propionaldehyde was singly deuterated (CH_2DCH_2CHO).

DISCUSSION

The oxidation of propylene or allyl alcohol to acrolein over metal oxide catalysts such as bismuth molybdate oxides is known to proceed through a symmetric intermediate such as the π-allyl species. This leads to equilibration of C-1 and C-3 in both the acrolein product (*15, 26*) and unreacted allyl alcohol (*15*). It is clear that such a mechanism is not operative in the conversion of *cis*-ALA-3-d_1 over Ag since only *cis*- and *trans*-ACR-3-d_1 were observed and not ACR-1-d_1 or *trans*-ALA-3-d_1. The absence of ACR-1-d_1 also precludes isomerization of ALA-3-d_1 to ALA-1-d_1.

The extent of randomization in the ACR-3-d_1 is very similar for the oxidation reaction of *cis*-ALA-3-d_1 over Ag and the repassage of *cis*-ACR-3-d_1. Therefore, it is reasonable to assume that the conversion of ALA in both the presence and absence of feed O_2 occurs with high retention of stereochemistry about the double bond while most of the randomization occurs subsequently during a separate readsorption of ACR. This would be consistent with the oxidation occurring via a dehydrogenation process which removes two H-atoms from

the $-CH_2OH$ moiety with little perturbation of the carbon–carbon double bond. These hydrogen atoms are then converted to H_2O in the presence of oxygen. However, when the oxygen levels are low presumably some of this hydrogen is scavenged or appears in the propionaldehyde product. The propionaldehyde is produced at least in part by hydrogenation of acrolein since ACR-d_1 added to the feed leads to propionaldehyde-d_1.

This description of the conversion of ALA to ACR as an oxidative dehydrogenation is similar to the mechanism inferred from isotopic labeling experiments with other alcohols by Madix and co-workers (*27, 28*). They examined the conversion of ethanol to acetaldehyde and methanol to formaldehyde over silver. It was inferred that an early step involved dissociative chemisorption through the oxygen atom producing an adsorbed RO moiety. Evidence for surface hydrogen was also inferred from the desorption of H_2(g).

While the mechanism for production of the ACR is presumably the same in the absence or presence of feed oxygen, there is nevertheless a change in the importance of the ACR readsorption–randomization process. At first inspection, the decreased importance of this process at high oxygen levels seems puzzling. It is well known from studies of the O_2–Ag–ethylene system that ethylene only adsorbs on an oxygenated surface (*29*). Madix *et al.* also found no evidence for adsorption of CH_3OH, C_2H_5OH, H_2CO, HCOOH, or $HCOOCH_3$ on a clean Ag(110) surface until oxygen was added (*27, 28, 30*). By analogy ACR should also adsorb better in the O_2-rich mixtures but simultaneously result in less randomization about the double bond. This paradox can be rationalized by recognizing that some readsorption of ACR may take place in the O_2-deficient reactions and that readsorption itself, which probably takes place through the oxygen atom, is a necessary but not sufficient condition for randomization about the carbon–carbon double bond.

It is difficult to avoid the conclusion that readsorption of ACR (or ALA) occurs to some extent even in the O_2-deficient mixtures. This is probably assisted by catalysts which have not been completely purged of oxygen. In contrast to the clean catalysts prepared by Madix *et al.* using ultra high vacuum techniques, there is evidence that Ag catalysts prepared with the reduction procedures and reaction conditions used in this study will contain residual oxygen (*31–33*). However, the ease or extent of the readsorption process for ACR must not be the only factor which influences the amount of randomization. It is attractive to also associate this with the presence and activity of the residual surface hydrogen which was postulated above for the reaction in the absence of feed-O_2. This reactive hydrogen would be involved in both proprionaldehyde production as well as the randomization of the ACR as both processes necessitate a perturbation of the π-system in the adsorbed ACR. Experiments by us to more definitively test these ideas were inconclusive. They were difficult to perform with reproducibility since they involved amounts of residual oxygen and hydrogen which were difficult to control.

In summary, the oxidation of ALA to ACR occurs by a mechanism with distinctly different intermediates compared to oxidation of propylene or ALA over metal oxide catalysts. Also, the randomization of stereolabeled acrolein-d_1 passed over a silver catalyst is greatest in the absence of feed-O_2. This presumably arises from a readsorption of acrolein and opening of the C–C double bond under such conditions, perhaps catalyzed by residual hydrogen.

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REFERENCES

1. "Allyl Alcohol. Technical Publication SC:46-32." Shell Chemical Corp., San Francisco, CA., 1946, 95 pp.
2. Azuma, R., Oiski, T., and Imoto, E., *J. Chem. Soc. Japan Ind. Chem. Sec.* **58,** 787 (1958).
3. Moureu, C., and Mignonac, G., *Compt. Rend.* **170,** 258 (1920).
4. Groll, H. P. A., and de Jong, H. W., U.S. Patent 2,042,220 (1936) to Shell Development Co.; French Patent 788,921 (1935) to N.V. de Bataafsche Petroleum Mij.
5. Constable, F. H., *Proc. R. Soc. (London)* **113A,** 254 (1926).
6. Sabatier, P., and Senderens, J. B., *Compt. Rend.* **136,** 983 (1903).
7. Murib, J. H., U.S. Patent 4,107,204 (1978) to National Distillers and Chemical Corp.
8. Sandonnini, C., and Quaglia, A., *Gazz. Chim. Ital.* **52,** I, 409 (1922).
9. Trillat, A., *Compt. Rend.* **133,** 822 (1901); *Bull. Soc. Chim.* **29,** 35 (1913); *J. Chem. Soc.* **1903,** 222.
10. Peytral, E., *Bull. Soc. Chim.* **29,** 39 (1921).
11. Delaby, R., *Compt. Rend.* **182,** 140 (1926).
12. Goldschmidt, S., Askenasy, P., and Grimm, H., *Ber.* **67,** 202 (1934).
13. Weston, P. E., and Adkins, H. J., *J. Amer. Chem. Soc.* **50,** 1930 (1928); **51,** 2430 (1929).
14. Sabatier, P., and Mailhe, A., *Compt. Rend.* **150,** 1217 (1910); *J. Chem. Soc.* **1910,** AI, 456.
15. Burrington, J. D., Kartisek, C. T., and Grasselli, R. K., *J. Catal.* **63,** 235 (1980).
16. Imachi, M., and Kuczkowski, R. L., unpublished results.
17. Cant, N. W., and Hall, W. K., *J. Catal.* **52,** 89 (1978).
18. Egashira, M., Kuczkowski, R. L., and Cant, N. W., *J. Catal.* **65,** 297 (1980).
19. Imachi, M., Egashira, M., Kuczkowski, R. L., and Cant, N. W., *J. Catal.* **70,** 177 (1981).
20. Bates, E. B., Jones, E. R. H., and Whiting, M. C., *J. Chem. Soc.* **1954,** 1854.
21. Murty, A., and Curl, R. F., Jr., *J. Chem. Phys.* **46,** 4176 (1966).
22. Larrabee, A. L., and Kuczkowski, R. L., *J. Catal.* **52,** 72 (1978).
23. Cherniak, E. A., and Costain, C. C., *J. Chem. Phys.* **45,** 104 (1966).
24. Wagner, R., Fine, J., Simmons, J. W., and Goldstein, J. H., *J. Chem. Phys.* **26,** 634 (1957).
25. Butcher, S. S., and Wilson, E. B., *J. Chem. Phys.* **40,** 1671 (1964).
26. Sachtler, W. M. H., and deBoer, N. H., *in* "Proceedings, 3rd International Congress on Catalysis, Amsterdam, 1964," p. 252. Wiley, New York, 1965; Adams, C. R., and Jennings, T., *J. Catal.* **2,** 63 (1963); Adams, C. R., and Jennings, T., *J. Catal.* **3,** 549 (1964); Adams, C. R., Voge, H. H., Morgan, C. Z., and Armstrong, W. E., *J. Catal.* **3,** 379 (1964); Grasselli, R. K., and Suresh, D. D., *J. Catal.* **25,** 273 (1972).
27. Wachs, I. E., and Madix, R. J., *Appl. Surface Sci.* **1,** 303 (1978).
28. Wachs, I. E., and Madix, R. J., *Surface Sci.* **76,** 531 (1978).
29. Kagawa, S., Iwamoto, M., Mori, H., and Seiyama, T., *J. Phys. Chem.* **85,** 434 (1981).
30. Barteau, M. A., Bowker, M., and Madix, R. J., *Surface Sci.* **94,** 303 (1980).
31. Hucknall, D. J., "Selective Oxidation of Hydrocarbons," p. 8. Academic Press, New York, 1974.
32. Czanderna, A. W., *J. Phys. Chem.* **68,** 2765 (1964).
33. Kilty, P. A., and Sachtler, W. M. H., *Catal. Rev. Sci. Eng.* **10,** 1 (1974).