

## Reply to Comments on the "Catalytic Conversion of Alcohols VI. Selectivity of Indium Oxide"

In the preceding letter Venkatasubramanian and Karuppannasamy (V&K) (1) criticize a mechanism we suggested for alcohol conversion over indium (2) and offer their mechanism. In Ref. (2), we modified Hauffe's dehydrogenation mechanism (3) of C $\alpha$ -H activation by: (a) emphasizing the concerted nature of the mechanism, (b) proposing that dehydrogenation and dehydration occur through the same intermediate, and (c) suggesting that dehydrogenation may occur through an enol transition state. We indicated that our mechanism, incorporating well-founded intermediates from organic chemistry to explain our selectivity for terminal alkenes, was very speculative.

Ingold reported, in 1927, the first of his many works which established the basis of a concerted mechanism in which, as described in his book (4), "the hydrogen atom and the electron attractor being bound to adjacent carbon atoms in the original molecule, atomic electron shells can remain complete through the change; and thus a co-operative effect arises: two bonds are broken, but each fission assists the other, the two constituting a single synchronised act." Saunders and Cockerill (5) describe the concerted mechanism in the more modern language of the variable transition state theory of E-2 reactions in which they emphasize that the balances and timing of the bond-making and bond-breaking process may vary with reactant structure and reaction conditions even though the mechanism remains a single-stage E-2 process with no detectable intermediate. The absence of a detectable intermediate has always been the feature which distinguished the con-

certed E-2 reaction mechanism from the stepwise E-1 mechanism.

To us, a concerted mechanism involves the chemisorption, and activation, of all atoms that will be eliminated. For dehydrogenation, the concerted mechanism requires synchronized adsorption by the hydroxyl hydrogen as well as the C $\alpha$ -H. In a similar manner, a common intermediate in a concerted mechanism for both dehydration and dehydrogenation requires adsorption by the C $\alpha$ -H, C $\beta$ -H, and the hydroxyl oxygen and hydrogen atoms with synchronized bond-breaking and bond-making to form the desorbed product. We readily admit that we should have placed stronger emphasis on this point in Ref. (2).

V&K interpret our mechanism to include "the initial adsorption of the C $\alpha$ -H as a hydride on the metal ion and a subsequent removal of a C $\beta$ -H to form a carbanion-like structure." Then they discuss individual equations, e.g., Eq. (3) of Ref. (2), as though we proposed these equations as steps in an E-1 elimination mechanism. However, we stated that, in our view, indium converts alcohols by a concerted mechanism but that we would, for clarity, write out mechanism in steps by Eqs. (1) and (4). Criticism of individual steps is unjustified since our concerted mechanism must be the sum of (1), (2), (3), (4), and (4') (Ref. (2)) acting in concert.

In their critical discussion, V&K present our data in a light which merits comment:

(1) V&K assert that poisoning should affect both reactions equally and interpret the change in dehydrogenation/dehydration selectivity with time (as given in

Table 4, Ref. (2)) to support their view that the two reactions need not occur via the same intermediate. (It is noted that V&K present, in their letter, a mechanism with a common intermediate leading to the two products.) When V&K attribute the change in reaction selectivity to poisoning they ignore our data in Fig. 1 (Ref. (2)) which show that the selectivity is altered by catalyst reduction. We repeatedly stated that india was reduced during the conversion of secondary alcohols. Since our data do not permit one to separate the effects of catalyst reduction from any catalyst poisoning, conclusions based on selectivity changes due to poisoning are invalid.

(2) We expressed concern about the temperature coefficients and only considered them, if equal, to be consistent with a common intermediate, not to be the basis for our mechanism.

(3) We find that the selectivity of thoria catalysts depends on sample preparation and pretreatment (6). We hesitate to interpret our results with thoria and india catalysts by the same mechanism.

(4) V&K assert that our data for india (in Tables 1 and 4, Ref. (2)) show that substitution of both  $\beta$ -carbons greatly slowed the rate of dehydration but not that of dehydrogenation. In reporting the data in Tables 1 and 4 we agreed with, and followed, a referee's suggestion that "in view of the uncertainties in temperature effects and poor reproducibility due to partial reduction, some of the tables should be shortened to show just the overall range in dehydration/dehydrogenation selectivity, 1-alkene/2-alkene selectivity, and *cis/trans* 2-alkene selectivity." Thus, the tables did not show that different catalysts and space velocities were used with 2- and 3-pentanol; hence, the difference in the amounts of dehydration and dehydrogenation must be viewed with caution. In Table 1 (Ref. (2)), the dehydration selectivity for 2-octanol conversion over two india samples, one precipitated from a chloride and the other from a nitrate solution, varied as much as

TABLE 1

Product Selectivity from the Conversion of Alcohols with Thoria Catalysts

Reactant	Percentage conversion to		Reference
	Olefin	Ketone	
2-Hexanol	80	4.0	(7)
3-Hexanol	10	5.0	(7)
3-Butanol	32	18	(8)
3-Pentanol	29	21	(8)

our data for 2- and 3-pentanol. Unreported selectivity data for 2-pentanol, using the same two india catalysts, was similar to that of 2-octanol.

It is true that Lundeen and van Hoozer (7) obtained very different selectivities for 2- and 3-hexanol (see Table 1). However, Thomke (8) obtained, in contrast to Lundeen and van Hoozer, about the same selectivities from the conversion of 2-butanol and 3-pentanol with a thoria catalyst. Clearly, the selectivity data for 2- and 3-alcohols (Table 1) must be viewed with caution.

(5) V&K point out that our mechanism cannot account for the rapid conversion of tertiary alcohols. On the basis of limited data, and in analogy with other oxide catalysts, a referee for Ref. (2) and I expected tertiary alcohols to be dehydrated more rapidly than secondary alcohols. Recently, we passed three tertiary alcohols over india and found that, under similar reaction conditions, about the same amount of dehydration was obtained with tertiary and secondary alcohols.

V&K propose, according to their text, a speculative concerted mechanism which includes an alkoxide species as an intermediate. V&K's revised mechanism differs from the one they presented in the first version of their manuscript. As we pointed out, combining the steps of their original mechanism gave a concerted mechanism similar to the one we proposed in Ref. (2). V&K's revised mechanism, outlined in their Eqs. (1),

(2), and (3), is not, as they state in their text, concerted; it could be made a concerted mechanism if the hydroxyl hydrogen was not detached to form the alkoxide as shown in Eq. (1). Even so, their revised mechanism does not provide a dehydration pathway to selectively form terminal alkenes from 2-ols. An adequate mechanism for an india catalyst must include a reason for selectively forming terminal alkenes.

In their revised mechanism, V&K show dehydrogenation occurring on adjacent metal atoms. As the india catalyst is reduced during use, the number of surface metal ions should increase with on-stream time. It appears to us that, because of this, V&K should predict an increase in dehydrogenation with on-stream time. However, when there is a significant change in selectivity, as in Fig. 1 and Table 1 (Ref. (2)), it is in the direction favoring dehydration, not dehydrogenation.

Thomke concluded, at about the same time as publication of Ref. (2), that his deuterium tracer studies showed that the formation of butene and ketone from 2-butanol with a thoria catalyst occurred through the same carbanion intermediate (8). In another publication, Noller and Thomke (9) report that, for several catalyst systems, the H/D exchange at both  $\beta$ -positions occurs at temperatures lower than those at which dehydration (or dehydrogenation) does. Thus, it may not be necessary to weaken the  $C^\alpha$ -H bond in order to activate the  $C^\beta$ -H bond leading to the terminal alkene; if this were the case there would be no compelling reason to propose the mechanism in Ref. (2). However, Noller and Thomke (9) believe that the H/D

exchange and the dehydration (or dehydrogenation) are independent reactions so that the reason for activation of the  $C^\beta$ -H bond in 2-ols leading to terminal alkenes remains uncertain.

We have obtained considerable data with many metal oxide catalysts since writing the manuscript for Ref. (2). We now suspect that, at least with some metal oxide catalysts, adsorbed oxygen ions and/or radicals play an important role in determining dehydrogenation-dehydration selectivity. This appears to be the case even for alumina (10), a material usually considered to be a very selective dehydration catalyst.

#### REFERENCES

1. Venkatasubramanian, N., and Karuppanasamy, S., *J. Catal.* **65**, 238 (1980).
2. Davis, B. H., *J. Catal.* **52**, 435 (1978).
3. Hauffe, K., *Advan. Catal.* **7**, 213 (1955).
4. Ingold, C. K., "Structure and Mechanism in Organic Chemistry," p. 421. Cornell Univ. Press, Ithaca, New York, 1953.
5. Saunders, W. H., Jr., and Cockerill, A. F., "Mechanisms of Elimination Reactions." Wiley, New York, 1973.
6. Davis, B. H., and Brey, W. S., Jr., *J. Catal.* **25**, 81 (1972).
7. Lundeen, A. J., and Van Hoozer, R., *J. Org. Chem.* **32**, 3386 (1967).
8. Thomke, K., *Z. Phys. Chem.* **196**, 225 (1977).
9. Noller, H., and Thomke, K., *J. Mol. Catal.* **6**, 375 (1979).
10. Davis, B. H., *J. Catal.* **26**, 348 (1972).

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