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LETTER TO THE EDITOR

Does *trans* Addition Occur after All?

In their recent elegant study of the hydrogenation, double-bond migration, and *cis–trans* isomerization of butenes, Yoon, Yang, and Somorjai propose an interesting mechanism (1). They propose that *cis*-2-butene undergoes *cis–trans* isomerization by first dehydrogenating to 2-butyne and then rehydrogenating to *trans*-2-butene. Thereby they raise an old stereochemical enigma wrestled with by two generations of catalytic chemists, and now a third. How can hydrogen add from a catalytic surface to opposite sides of an adsorbed species?

Not that evidence for apparent *trans* addition is lacking. Such evidence is most easily observed during the hydrogenation and deuteriumation of tetrasubstituted alkenes, in particular small ring cycloalkenes such as 1,2-dimethylcyclohexene (2). And examples of apparent *trans* addition continue to be reported in current synthetic literature (3). Moreover, the phenomenon is not unique to hydrogenation of alkenes; parallel examples occur during the deuterium exchange of small rings over noble metal catalysts (4) and during the racemization and deuterium exchange of (+)-3-methylhexane over Ni (5) and Pd (4). However, rarely has *trans* addition been invoked in cases of alkyne hydrogenation. As in the pioneering work of Rabinovitch (6), the *cis*-alkene is usually assumed first formed followed by isomerization to the *trans* through the classical associative mechanism of Horiuti and Polanyi (7).

Over the years, almost every conceivable explanation has been proposed for apparent *trans* addition and apparent *trans* exchange. Briefly, these are a dissociatively adsorbed alkene (8), a rollover mechanism (6) [and the similar alkylidene species (9)], a topside addition of hydrogen (10), a 1,3 hydrogen shift over the topside of an adsorbed alkene (11), and double-bond migration followed by desorption and readsorption (the classic mechanism) (12). This last mechanism (which is one of the two mechanisms considered by the current authors but rejected) seems to be the most widely accepted mechanism, probably because it employs relatively simple known mono- and diadsorbed alkyl surface species and well-known conformational changes involving rotation about C–C single bonds. On the other hand, explaining apparent *trans* addition to alkynes presents a formidable stereochemical problem because conformational changes are restricted in the resulting alkene and if hydrogen adds only from the surface, the *cis*-alkene is preferred (13).

In the classic explanation, absence of the required double-bond isomers is explained on the basis of their stronger adsorption and more rapid hydrogenation. Such an argument in the present case would stress that *cis*-2-butene may indeed isomerize through a 1,2-diadsorbed species which is more strongly adsorbed and more rapidly hydrogenated than either of its 2,3-diadsorbed isomers, so desorbed 1-butene would not be expected. Deuteriumation studies on the same catalysts would help authenticate a mechanism involving 1-butene especially if deuterium is found at C_1. However, isomerization need not pass through the 1,2-diadsorbed state; rather, as the authors point out, it may simply follow the classic mechanism by forming the half-hydrogenated state and eliminating the hydrogen geminal to the one added. During deuteriumation this isomerization from the less stable to the more stable isomer traps deuterium at the rotated carbon (14). Thus isomerization of *cis* under deuterium should produce monodeutero *trans*.

The authors, however, present evidence that the rate of *cis*-to-*trans* isomerization is twice as fast on stepped Pt(755) as on any of Pt foil, Pt(111), or Pt(100). So, if one accepts the classic argument, an explanation must be offered for why isomerization to *trans*-2,3-diadsorbed butane occurs faster on this stepped surface than on a plane. Nobody has had reason to worry about that until now. On the other hand, if one accepts the proposed dehydrogenation–rehydrogenation mechanism, an explanation must be offered for the gymnastic feat performed by the adsorbed 2-butyne and the surface hydrogen.

Although not specified, the authors' postulated mechanism must involve a dissociatively adsorbed alkene first proposed by Farkas and Farkas (15). That being the case, a mechanism that would satisfy the stereochemical requirements might be one in which one surface hydrogen adds from below the adsorbed 2-butyne (perhaps it is 2,3-diadsorbed-*cis*-butene now) to form a monoadsorbed 2-butene followed by a hydrogen hopping off a ledge, as proposed by Bond (16), onto the top of the monoadsorbed 2-butene on the plane below (Fig. 1). Under deuterium, this should produce *trans*-2,3-dideutero-2-butene.

Another way to add hydrogen on top has recently been demonstrated. On Cu(100), hydrogen atoms generated in the gas phase have been shown to add to the top side of an adsorbed alkene (17). Thus, a surface hydrogen atom may add to the surface side and a gas-phase hydrogen atom

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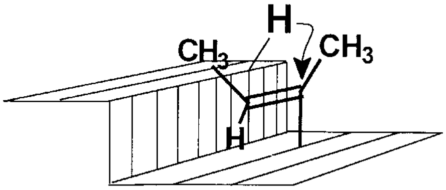

FIG. 1. Difficulty of *trans* addition to dissociatively adsorbed *cis*-2-butene (half-hydrogenated 2-butyne) at a step.

may add to the top side. Therefore, if hydrogen atoms were formed somewhere in the reaction chamber, they might add to the top side to accomplish *trans* addition. On the other hand, it should be pointed out that although hydrogen atoms add to the topside of adsorbed alkenes, their addition to the topside of adsorbed alkynes presents the problem of inversion at an sp^2 hybridized carbon as shown in Fig. 1.

None of these mechanisms is completely satisfactory, so a new mechanism might be considered. This mechanism must now account for the geometry of the surface. If Pt(755) steps catalyze *cis–trans* isomerization faster than planes, then they must furnish some unique site not found on planes. These might be called B_4 sites according to the nomenclature of van Hardeveld and Hartog (18). That is, they furnish four nearest neighbors for coordination. Rarely do we have such a well-characterized site associated with a specific reaction. This reaction may occur by three mechanisms: addition–rotation–elimination (the classic mechanism), dissociation–*trans* addition (as the authors propose), and simple rotation. This last mechanism is inhibited by an energy barrier associated with the π bond (19). However, if *cis*-2-butene adsorbs such that association with the B_4 metal atoms weakens the π bond and lowers the energy barrier, rotation about C_2–C_3 will be driven by repulsion of the methyl groups and the greater stability of the *trans* isomer. As this occurs, one carbon atom of the double bond may interact with a plane atom and the other with a step atom such that the adsorbed species is already partway to the *trans* form (Fig. 2). Experimentally, *cis–trans* isomerization at this site during deuteriumation should occur without incorporation of deuterium. This may be difficult to observe, however, because *cis–trans* isomerization by the classic mechanism should be occurring simultaneously on plane sites and thereby incorporating one deuterium per isomerization.

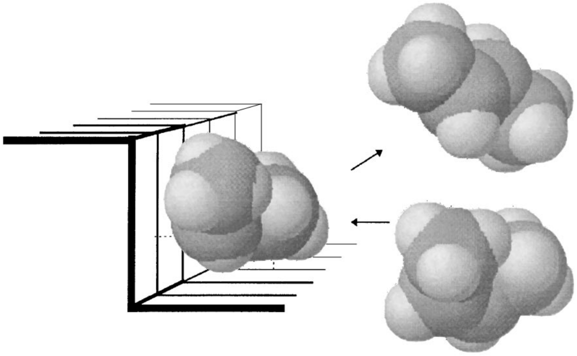

FIG. 2. Proposed *cis–trans* isomerization site.

The probability of such sites existing on nanometer-size crystallites of working catalysts is low since their surfaces will likely be convex and exhibit edges but not steps. The exception would be small crystallites with partial overlayers that create B_5 sites (18). However, since most catalysts used by many laboratories, especially academic, contain large particles, for example, 5% Pd/C and 5% Pt/C, which expose mostly planes, the probability of such sites resulting from partial overlayers on these is larger than on small crystallites. It would be interesting to see if the B_5 sites on a Pt(443) or a Pt(331) surface (20) also exhibit faster rates for *cis–trans* isomerization.

Although the B_4 site gives no kinetic advantage to addition (the authors report the same rate for all surfaces), the fact that alkenes may adsorb in this configuration suggests the possibility that surface hydrogens may add to both sides of the double bond, one from the ledge and one from the plane. Likewise, adsorption of *cis*-2-butene at this site may result also in dehydrogenation to a π-adsorbed 2-butyne followed by *trans* addition of surface hydrogen, as the authors seem to propose. Although it is not clear why this should occur faster than the rotation mechanism suggested, it does offer an explanation for formation of desorbed alkynes cited by the authors.

Going a step further and considering the general topic of *trans* addition lead to the problem that groups larger than hydrogen may inhibit the $C{=}C$ double bond from approaching close to the B_4 site. Thus, tetrasubstituted alkenes, such as 1,2-dimethylcyclohexene, may be inhibited from adsorbing directly on this site. However, its isomer, 2,3-dimethylcyclohexene, may be able to nestle in close enough to allow *trans* addition (Fig. 3). Similarly, it is worth noting that many examples of apparent *trans* addition involve a methyl attached to the double bond [$\Delta^{9(10)}$-octalin (21) being a notable exception]. In such cases, the double bond might migrate to the methyl group and form a 1,1-diadsorbed alkylidene at the step, which would allow addition of hydrogen to either side (Fig. 4).

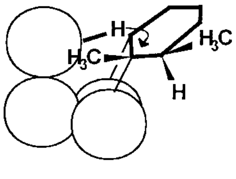

FIG. 3. *trans* addition to 2,3-diadsorbed 1,2-dimethylcyclohexane at a B_4 site.

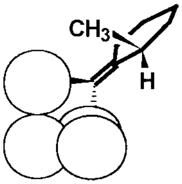

FIG. 4. B_4 adsorbed alkylidene formed from double-bond migration in 1,2-dimethylcyclohexene.

Whatever the explanation, it is important to point out that this discovery of structure sensitivity for *cis*-to-*trans* isomerization on Pt(755) reveals a surface structural feature which calls for an expanded way of thinking about alkene interactions with surfaces.

A surface site on Pt(755) has been clearly associated with *cis*–*trans* isomerization of *cis*-2-butene. Although the authors' proposed mechanism of dehydrogenation–rehydrogenation is a possibility, an alternative mechanism should be considered. In this mechanism, *cis*-2-butene adsorbs at B_4 ledge sites where interaction with several metal atoms lowers the π-bond energy enough to allow rotation about the C_2–C_3 bond to form *trans*-2-butene. Identification of such a site offers a possible explanation for apparent *trans* addition to alkenes and apparent *trans* exchange of alkanes.

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