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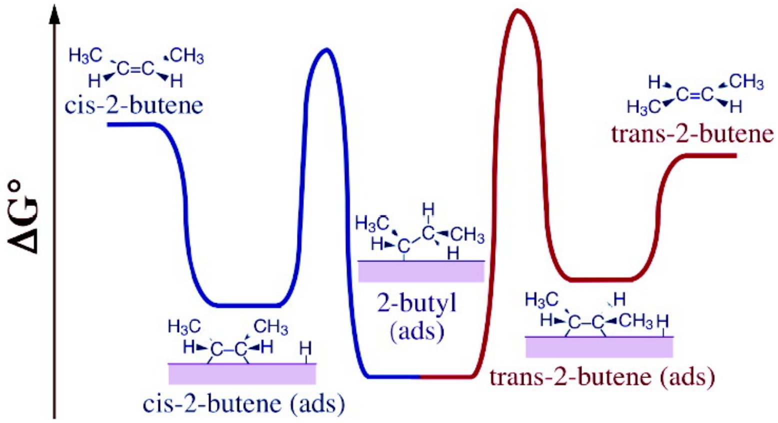

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Selectivity in Platinum-Catalyzed cis−trans Carbon−Carbon Double-Bond Isomerization

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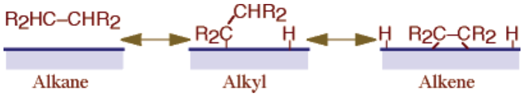
Although the conversion of alkenes by transition metals is one of the oldest and more studied catalytic reactions,[1−3] some key issues remain unresolved still. In particular, it is not clear what controls selectivity toward the formation of cis versus trans olefins.[4,5] The answer to that question has significant practical implications because, for instance, it is desirable to reduce the production of trans fatty acids during the partial hydrogenation of natural oils to edible fats.[6,7]

Most C═C double-bond hydrogenation, dehydrogenation, H−D exchange, and isomerization reactions involve the series of reversible steps described by the so-called Horiuti−Polanyi mechanism (Scheme 1).[8] According to this deceivingly simple scheme, selectivity between cis and trans alkene formation is explained by the stereospecificity of the removal of a hydrogen atom from the β position of the alkyl surface intermediate.[9] This has been quite difficult to probe in the past because (1) alkyl surface species are fairly reactive and therefore not easy to isolate,[10] and (2) most analytical techniques cannot discriminate between cis and trans isomers.[11] In particular, because both isomers yield virtually identical mass spectra,[12] their separation in temperature-programmed desorption (TPD) studies is nearly impossible. Fortunately, each H−D isotope exchange in olefins is accompanied by a cis−trans isomerization, so the former can be used as proxy for the latter. This approach has allowed us to investigate the mechanism of cis−trans isomerizations on model catalytic surfaces directly.

Scheme 1. Horiuti−Polanyi Mechanism



TPD and reflection−absorption infrared spectroscopy (RAIRS) experiments were carried out on a Pt(111) single crystal using a ultrahigh vacuum (UHV) chamber equipped with quadrupole mass and Fourier transform infrared spectrometries.[13,14] The platinum crystal was spot-welded to the supporting manipulator via tantalum wires connected to a liquid nitrogen reservoir in order to be able to cool and/or resistively heat the sample to any temperature between 90 and 1200 K (as monitored by a chromel−alumel thermocouple spot-welded to the edge of the crystal). The surface was cleaned periodically by cycles of O_2 treatment, Ar^+ bombardment, and 1200 K annealing until no impurities were detected. A linear heating rate of 10 K/s was used in the TPD experiments, and the partial pressures of up to 15 masses were recorded in each TPD run by using an interfaced computer in order to confirm the identity of the desorbing species. The *cis*- and *trans*-2-butenes (>95% purity) and deuterium (>99.5% atom purity) were purchased from Matheson, and hydrogen (>99.995% purity) was obtained from Liquid Carbonic. The purity of all those gases was routinely checked by mass spectrometry. All gases were dosed by backfilling of the vacuum chamber while keeping the surface temperature below 100 K. The ensuing coverages are reported in Langmuirs (1 L = 1 × 10^{-6} Torr•s), not corrected for ion gauge sensitivities.

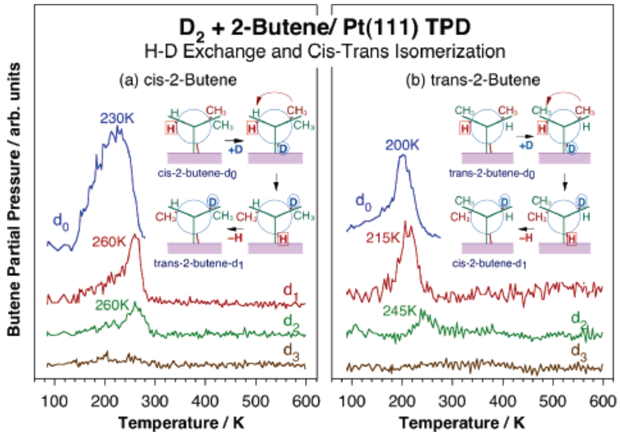


Figure 1. TPD spectra from 2.0 L of *cis*- (left) and *trans*- (right) 2-butenes adsorbed on Pt(111) surfaces predosed with 50 L of D_2. Shown are the traces for the molecular desorption of the original butenes (d_0) as well as for the mono- (d_1), di- (d_2), and tri- (d_3) substituted products produced by H−D exchange reactions. The insets show the sequences of Newman projections that explain the association of each isotope exchange with a cis−trans isomerization.

Figure 1 shows TPD data for the H−D isotope exchange that takes place in adsorbed *cis*- (left) and *trans*- (right) 2-butenes upon thermal activation on deuterium-predosed Pt(111). No more than two hydrogen substitutions are seen in either case, indicating that exchange occurs only at the C═C double-bond positions in both molecules. On the other hand, each isomer displays its own distinct isotope exchange kinetics, a fact highlighted by the different peak shapes and peak positions seen in Figure 1 for the several desorbing products. For instance, while molecular *trans*-2-butene desorbs around 200 K, *cis*-2-butene detection peaks at 230 K instead. This means that the former is less tightly bound to the surface than the latter (11.6 vs 13.4 kcal/mol). Also, the 2-butene-d_1 produced from the trans isomer desorbs at approximately the same temperature as the nonsubstituted reactant (both d_0 and d_1 traces in the right panel of Figure 1 display similar shapes), whereas it is detected around 260 K with *cis*-2-butene, at the tail end of the molecular desorption. Finally, 2-butene-d_2 is produced at the same temperature as 2-butene-d_1 in the cis case, but at a higher temperature with the trans isomer.

To explain these observations, it is important to realize that each H−D exchange in the adsorbed olefin is accompanied by a concurrent cis−trans double-bond isomerization. This is illustrated by the sequences of Newman projections provided in the respective insets of Figure 1. There, it is seen that the removal of a hydrogen atom from the alkyl intermediate produced by deuterium addition into the initial olefin requires a rotation around the original carbon−

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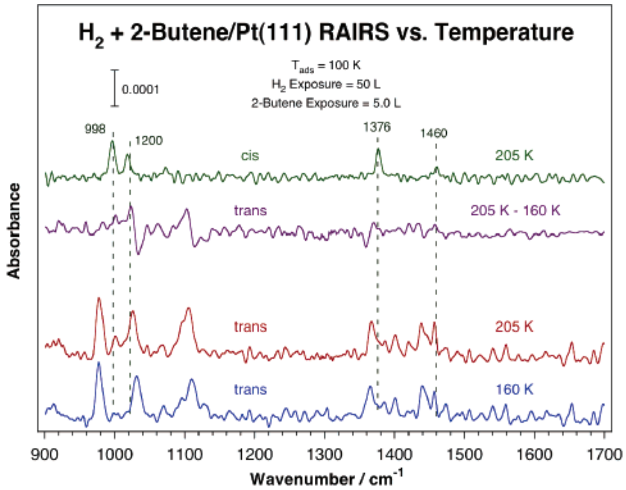

Figure 2. RAIRS from 5.0 L of 2-butene adsorbed on 50 L of H_2-predosed Pt(111). The bottom two traces are for the trans isomer annealed to 160 and 205 K, respectively, while the top two compare the resulting (205 − 160 K) difference spectrum with that of *cis*-2-butene at 205 K. The new peaks at 998, 1200, 1376, and 1460 cm^{-1} in the difference trace point to a trans-to-cis isomerization below 205 K.

carbon double bond, forcing one of the methyl groups to switch sides in the final product. In that light, it can be concluded from the TPD data in Figure 1 that the isomerization from *trans*- to *cis*-2-butene (as seen by the desorption of 2-butene-d_2 in the experiment with *cis*-2-butene and of 2-butene-d_1 with *trans*-2-butene) is easier, that is, takes place at lower temperatures than the reverse conversion from the cis to the trans isomer (indicated by the 2-butene-d_1 and -d_2 TPD traces for the *cis*- and *trans*-2-butenes, respectively). This is consistent with the stronger adsorption observed here for *cis*-2-butene, but not with the thermodynamic data for the gas-phase species ($\Delta H_{f,298}^{\circ} = -2.67$ vs -1.67 kcal/mol for *trans*- and *cis*-2-butene, respectively).[15] Clearly, the selectivity toward *cis*-2-butene formation seen in our TPD data is kinetically controlled.

The chemistry reported above was also followed by RAIRS. Each H−D exchange step was easily identified by the appearance of a new C−D stretching mode, at 2065 cm^{-1}, upon heating the adsorbed *cis*-2-butene to 220 K and at 2060 and 2078 cm^{-1} upon heating the *trans*-2-butene to 190 and 280 K, respectively (data not shown). The cis−trans transformations could also be probed independently by experiments with coadsorbed hydrogen instead of deuterium. Figure 2 displays the appropriate data for the first *trans*- to *cis*-2-butene isomerization and specifically shows the good match between the new peaks that develop at 998, 1200, 1376, and 1460 cm^{-1} upon heating the adsorbed *trans*-2-butene to 205 K and those of the cis isomer adsorbed at the same temperature. Similar transformations were observed for the other isomerizations (data not shown).

The main conclusion from these results is that trans olefins isomerize to their cis conformers on Pt(111) surfaces at a rate significantly faster than the other way around. The data suggest that this difference is due, at least in part, to an increase in stability of the cis isomer upon adsorption (see the energy diagram in the graphical abstract). It could be argued that the interaction of the groups attached to the $C{=}C$ double bond of the olefin (methyl groups in the case of the 2-butenes) with the surface destabilizes the adsorbate, and that in the case of cis olefins, that alkyl (methyl) surface repulsion can be minimized by tilting of the molecular plane away from a flat configuration. Since the trans isomer has alkyl (methyl) groups on both sides of the molecule, such geometrical rearrangement would not provide any relief for that interaction.

A comparison of the relative intensities of the RAIRS peaks for the symmetric versus asymmetric methyl deformation modes does indeed point to a more upright orientation of the CH_3 moieties in the adsorbed cis isomer (data not shown). Moreover, published X-ray absorption spectroscopy data show that the C−C bond length in the adsorbed *cis*-2-butene is significantly longer than that in the trans isomer.[17] This can be interpreted as the consequence of a more extensive rehybridization from π to di-σ bonding to the surface, a change that is typical in olefins and that is accompanied with an increase in binding energy.[18,19] On the other hand, density functional theory (DFT) calculations proved to be of insufficient accuracy to provide further insight on this issue.[16] In any case, if steric factors do affect the stability of adsorbed olefins and, consequently, the kinetics of their cis versus trans conversion, this would be expected to be the most pronounced on close-packed surfaces, such as the (111) plane used here, and less significant on more open structures. Pointedly, a recent kinetic study on the catalytic conversion of butenes on single-crystal surfaces reported a ratio of room temperature isomerization-to-hydrogenation rates of only ∼9% on Pt(111) and Pt(100), but of over 20% on the more open Pt(755).[20] A systematic study of the effect of surface structure on cis−trans isomerization selectivity is currently underway in our laboratory.

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