

Change in Reaction Pathway Induced by Deuteration: Thermal Decomposition of Neopentyl Groups on Pt(111) Surfaces

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Previous surface science studies on the chemistry of alkyl groups on various metal surfaces have revealed that their thermal decomposition often involves an initial β -H elimination step, in a fashion similar to that of alkyl ligands in organometallic compounds, to produce the corresponding alkene and surface hydrogen.¹ Since in most cases this β -H elimination reaction is dominant, much less is known about other hydrocarbon reactions such as α - or γ -H eliminations or C–C bond scission steps. The thermal decomposition of adsorbed neopentyl groups [(CH₃)₃CCH₂–], which do not have hydrogen atoms at the β position, can provide more information about those less common reactions. In this paper we present temperature-programmed desorption (TPD) data for nondeuterio- [(CH₃)₃CCH₂–], α -deuterio- [(CH₃)₃CCD₂–], γ -deuterio- [(CD₃)₃CCH₂–], and perdeuterio- [(CD₃)₃CCD₂–] neopentyl groups adsorbed on Pt(111) surfaces. It was found that in the decomposition of both α - and γ -deuterated neopentyl iodides a hydrogen, not deuterium, is eliminated first. This indicates that while γ -H elimination takes place in the former case, α -H elimination occurs in the latter system instead. It is suggested that such a change in reaction path is due to the kinetic isotope effect associated with the deuterium substitution, which makes the reactions involving deuterium atoms slower. This explanation implies that the rates of the α - and γ -H elimination reactions are probably of the same order of magnitude, since their difference must be less than the changes caused by deuterium substitution.

The TPD experiments were performed in an ultra-high-vacuum chamber pumped to a base pressure below 10⁻¹⁰ Torr and equipped with an ion sputtering gun for cleaning of the sample, a UTI-100C mass spectrometer for temperature-programmed desorption experiments, and a Mattson Sirius 100 FT-IR spectrometer for reflection-absorption infrared spectroscopy (RAIRS).^{2,3} The mass spectrometer was controlled by a personal computer, in a setup that allowed for the simultaneous data collection of up to 15 masses. A moveable cone was mounted on the top of the mass spectrometer to minimize the signals from both the background gases and the desorption from the sample holder. The (isotopically labeled) neopentyl groups were produced by thermal decomposition of the respective neopentyl iodides on the Pt surface; RAIRS spectra show definite changes associated with the breaking of the C–I bond upon increasing the adsorption temperature of the neopentyl iodide from 115 to 170 K.⁴ The nondeuterio-neopentyl iodide was purchased from Aldrich (98% purity) and used as supplied, the α -deuterio-neopentyl iodide was synthesized by reduction of trimethylacetyl chloride (Aldrich, 99%) with LiAlD₄ (Aldrich, 98 D-atom %) to α -deuterio-neopentyl alcohol⁵ and subsequent iodine substitution,⁶ and the γ - and perdeuterio-neopentyl iodides were prepared from acetone-*d*₆ (Aldrich, 99.5 D-atom %), via pinacolone-*d*₁₂, γ -deuteriotrimethyl acetic acid,^{7,8} and either γ -

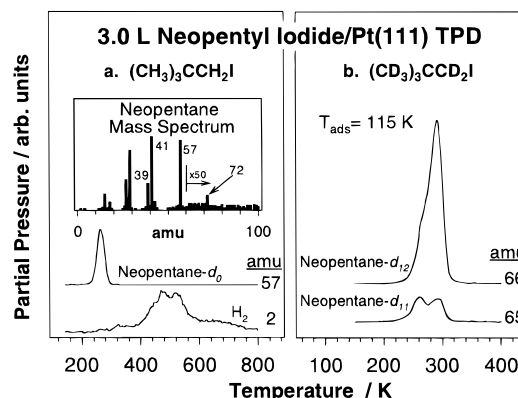


Figure 1. Left: Temperature-programmed desorption from 3.0 L of nondeuterio-neopentyl iodide adsorbed on Pt(111) showing the desorption of the main products, namely neopentane (57 amu) and hydrogen (2 amu). Left, inset: Mass spectrum for normal neopentane. Right: Neopentane temperature-programmed desorption from 3.0 L of perdeuterio-neopentyl iodide on Pt(111). The high intensity of the 66-amu signal shows that the neopentane produced in this case is mainly C₅D₁₂.

or perdeuterio-neopentyl alcohol.⁵ The purity of the vapors was checked by mass spectrometry in situ in the vacuum chamber. Doses are reported in langmuirs (1 L \equiv 10⁻⁶ Torr·s).

Figure 1 displays typical TPD spectra for the decomposition of neopentyl groups on Pt(111). The left panel of that figure shows the hydrogen (2 amu) and neopentane (57 amu) TPD traces obtained after a 3.0 L dose of nondeuterio-neopentyl iodide on the surface; those were the only two desorption products observed in this case (molecular desorption occurs at 185 K, but only after exposures above 5.0 L). The hydrogen desorption that occurs between 400 and 600 K is typical for decomposition of surface hydrocarbon fragments, and the trace for the 57 amu is accompanied by similar signals for 43, 41, 39, and 29 amu (not shown), with relative intensities matching those for neopentane (Figure 1, inset). It is important to notice here that the intensity of the parent molecular peak of neopentane (72 amu) is more than 100 times weaker than that of the *tert*-butyl fragment (57 amu),^{9,10} and could therefore not be resolved in our TPD experiments.

The right panel of Figure 1 shows the desorption traces for 65 and 66 amu obtained in TPD experiments with 3.0 L of perdeuterio-neopentyl iodide: the 66 amu signal is clearly the most intense, which means that perdeuterio-neopentane, C₅D₁₂, is preferentially formed in this case. This neopentane must form via the reductive elimination of surface neopentyl groups with the deuterium atoms that originate from dehydrogenation of other neopentyl fragments, which means that the first step in the decomposition of neopentyl groups can be identified by monitoring the deuterium content of the neopentane formed in the TPD experiments with partially deuterated neopentyl iodides. In addition, the low intensity of the 65-amu trace in Figure 1 indicates that the amount of neopentane produced by reaction with background hydrogen is relatively small. The two peaks observed in this desorption trace point to isotope effects in the decomposition and hydrogenation reactions of the neopentyl moieties.

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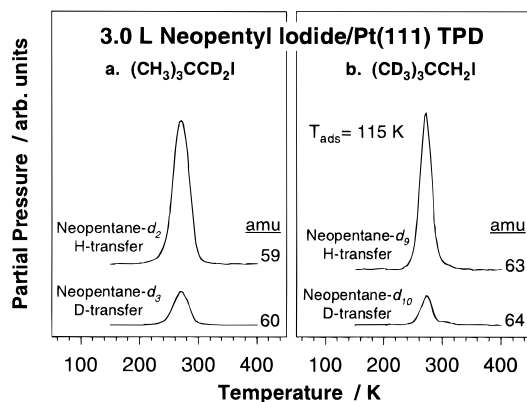


Figure 2. Neopentane temperature-programmed desorption from 3.0 L of α -deuterio- (left) and γ -deuterio- (right) neopentyl iodide adsorbed on Pt(111). The neopentane is in both cases formed via a hydrogen, not deuterium, transfer.

Figure 2 summarizes the most important neopentane desorption traces obtained in TPD experiments with 3.0 L of α - (left) and γ - (right) deuterio-neopentyl iodides. In the case of α -deuterio-neopentyl iodide the most intense signal is that for 59 amu, indicating the predominant desorption of neopentane- d_2 . This means that the formation of this neopentane mainly involves hydrogen, not deuterium atoms, implying that the first step in the decomposition of α -deuterio-neopentyl groups is a γ -H elimination step (which is presumably accompanied by the formation of a 3,3-dimethylplatinacyclobutane species on the surface). The low intensity seen for the 60-amu trace may be due to a small amount of deuteration, which would imply that either some α -D elimination takes place as well or some previous H/D exchange occurs within the surface species. The most intense peak in TPD experiments with the γ -deuterio-neopentyl iodide, on the other hand, is that for the 63 amu, indicative of the formation of neopentane- d_9 . Quite remarkably, a hydrogen atom is transferred in this case too, which means that, in contrast to the case of the α -deuterio-neopentyl species, the first step in the γ -deuterio-neopentyl decomposition is an α -H elimination reaction (probably leading to the formation of surface neopentylidene groups). The intensity of the 64-amu peak can again be caused by either γ -D elimination or H/D exchange.

A possible explanation for the different reaction paths for α - and γ -deuterio-neopentyl groups is that the kinetic isotope effect associated with deuterium substitution controls the selectivity of the reaction: since reactions involving deuterium atoms are expected to be slower than those with hydrogen, H-elimination

steps must dominate regardless of the position of the hydrogen atoms in the molecule. Based on rate ratios from the data in Figure 2, the isotope effect for the hydride elimination steps was estimated to be between five and ten (factors larger than ten have in fact been reported for the dissociation of the neopentane ligand in $(C_p^*Rh(CO)(CH_3)_4C$ to neopentyl and hydride ligands at temperatures below 200 K).¹¹ The same calculations also indicated that the rate constant for α -H elimination is about five times larger than that for γ -H elimination, but since the latter is statistically more favorable than the former (there are nine γ and only two α hydrogens in neopentyl moieties), the two rates end up being about the same (within 15% of each other).

Such a change in decomposition pathway induced by deuteration was not observed in the decomposition of dineopentylbis(triethylphosphine) platinum(II), where γ -H elimination was preferred in both the α - and γ -deuterated neopentyl groups instead.¹² A different behavior was also observed on Ni(100) surfaces, where α -H elimination, which is the preferred reaction,¹³ is followed by a subsequent C–C bond scission reaction to isobutene;¹⁴ this latter reaction was not observed on the Pt(111) surface.

3,3-Dimethylplatinacyclobutane is an example of the type of metallacycles that may result from the α,γ -coordination of hydrocarbon moieties believed to occur during the catalytic hydrogenolysis and isomerization of alkanes.¹⁵ The data presented in this paper strongly suggest the formation of a α,γ -diadsorbed species on Pt(111) in the case of neopentyl moieties on Pt(111), though this reaction seems to compete with the production of neopentylidene species. Our data are also consistent with the relatively high selectivity toward the formation of neopentane- d_1 to - d_3 in H/D exchange processes over supported Pt catalysts, which can be achieved via a neopentylidene intermediate, compared to the production of neopentane- d_4 to - d_9 , which involves an α,γ -diadsorbed intermediate.^{15,16}

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