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Identification of a Novel π + σ Bonded η⁷-Benzyl Species from Toluene Adsorption on Pt(111) at 350 K

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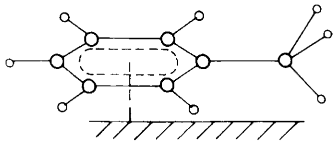
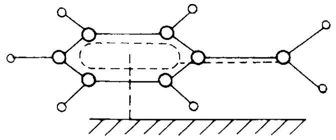
Electron energy loss and thermal desorption spectroscopies have been used to show that at 300—350 K toluene adsorbed on a Pt(111) surface is selectively dehydrogenated to give an adsorbed η^7-benzyl which is π-bonded through the arene and σ-bonded through the methylene side group.

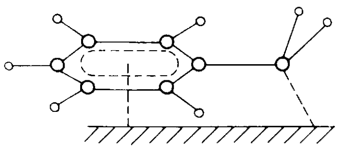
In this communication, high resolution electron energy loss (E.E.L.) and thermal desorption (T.D.) spectroscopies are used to show that on a Pt(111) surface at 300—350 K, toluene [$C_6H_5CH_3$ (h_8), $C_6D_5CH_3$ (d_5h_3), and $C_6D_5CD_3$ (d_8)] is partially dehydrogenated to give an adsorbed η^7-benzyl species which is π-bonded through the aromatic ring and σ-bonded through the methylene side group.

At <300 K, toluene adsorbed non-dissociatively to give E.E.L. spectra with vibrational bands which could satisfactorily be divided into modes due to an unperturbed methyl group (stretch, deformation, and rock) and a parallel π-bonded arene. For the latter, the increase in frequency of the strong γ(CH) mode on adsorption [$730 \rightarrow 840$ cm^{-1} (h_8) and $560 \rightarrow 620$ cm^{-1} (d_5h_3 and d_8)] and unsaturated CH stretch [3020 cm^{-1} (h_8) and 2250 cm^{-1} (d_5h_3 and d_8)] are diagnostic of π-bonding of 6-electron aromatics in both arene molecular complexes and strong heterogeneous adsorption on metals.[1,2] As a result of the parallel η^6-bonding of the ring, structure (I), the in-plane vibrational modes are largely screened and relatively simple E.E.L. spectra are seen.

The T.D. spectra showed parent toluene peaks at 315 and 445 K, and irreversible hydrogen evolution in a desorption-limited pulse at 325 K (region A) followed by a broad reaction-limited region with peaks at 480 and 640 K (regions B and C). These later regions of hydrogen desorption may be associated with the destructive dehydrogenation, including C–C bond rupture, of the adsorbed species while region A corresponds to partial dehydrogenation of the initially adsorbed species without rupture of the carbon skeleton.[3] The ratio of hydrogen desorbing in regions A:(B+C) was 1:7 indicating an intermediate adsorbed species of composition C_7H_7. The T.D. spectrum from $C_6D_5CH_3$ adsorption showed that the single region A hydrogen atom desorbing per adsorbed η^6-toluene originated selectively from the methyl group to produce an adsorbed benzyl species. On Pt(100), Ni(111), Ni(100), Ni[9(111) × (111)], and Ni [7(111) × (310)] surfaces,


(I)


(II)


(III)

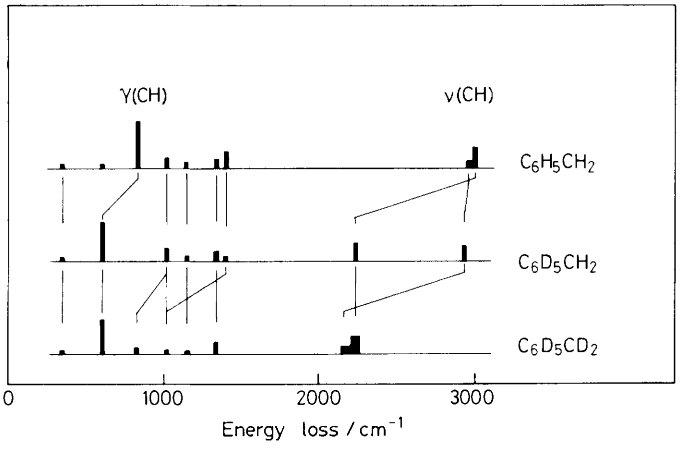


Figure 1. E.E.L. spectra of η^7-benzyl h_7, d_5h_2, and d_7 species adsorbed on Pt(111) formed by annealing adsorbed toluene to 350 K.

Muetterties and co-worker[4,5] similarly have noted that toluene selectively dehydrogenates the alkyl group at lower temperatures. Similar processes on Pt(111)[6] and Ni(110)[5] could not be detected. These workers proposed, without residual stoicheiometry estimates or spectroscopic evidence, that an adsorbed planar benzyl species was formed in which the methylene side-group was sp^2 hybridised in order to achieve a perceived favourable delocalisation of the seven p_π electrons of the C_7 skeleton, structure (II). An alternative configuration not considered by these workers is shown in (III) and involves a similar parallel-bonded C_7 skeleton but with π-bonding of only the six-ring p_π electrons and σ-bonding of the methylene group, which accordingly should be nearly sp^3 hybridised. A sensitive molecular vibrational spectroscopy like E.E.L. spectroscopy is ideally suited to distinguish between these possibilities. A summary of the E.E.L. spectra taken after annealing adsorbed toluene (h_8, d_5h_3, and d_8) to 350 K is shown in Figure 1. The strong γ(CH) bending modes are seen at 840 cm^{-1} (h_7) and 605 cm^{-1} (d_5h_2 and d_7) and along with the unsaturated CH stretches [3010 cm^{-1} (h_7) and 2240 cm^{-1} (d_5h_2 and d_7)] and relative simplicity of the spectra are indicative of strong parallel π-bonding of the aromatic ring in a manner similar to that seen for non-dissociatively adsorbed toluene itself. Central to the aim of this study is the determination of the hybridisation of the methylene side group and with it the mode of bonding of the adsorbed benzyl. The most sensitive test for this is the CH(D) stretching frequencies which may be expected at 3000—3100 cm^{-1} (>2200 cm^{-1}) for sp^2 hydridisation and <3000 cm^{-1} (<2200 cm^{-1}) on saturation. As a result of the relatively poor resolution of E.E.L. spectroscopy (typically ~50 cm^{-1} in the present study) the ring and methylene CH(D) stretching bands of the per-protio- and per-deuterio-species are not resolved although conspicuous shoulders at < 3000 and < 2200 cm^{-1} respectively hint at some degree of saturation. More decisive is the spectrum of $C_6D_5CH_2$ where these bands are isotopically separated. Here the ring CD component at 2240 cm^{-1} is consistent with unsaturation of the π-bonded arene while the CH_2 component, peaking at 2940 cm^{-1}, is unequivocal evidence for a saturated methylene side group as required by bonding configuration (III). For comparison, an alkane methylene gives stretches at 2850 cm^{-1} (sym) and 2920 cm^{-1} (asym) which shift to 2866 and 2960 cm^{-1} respectively in the strained cyclopentane ring.

The $\sigma + \pi$ bonding configuration of the η^7-benzyl on Pt(111) arises from intrinsic 6-electron aromaticity of the arene while the methylene side group is σ-bonded to the surface more or less independently in a manner reminiscent of the rehybridised configuration of low temperature (<250 K) di-σ-adsorption of alkenes on Pt(111).[7] This $\sigma + \pi$ bonded η^7-benzyl species derived from toluene adsorption on a Pt(111) surface at ~350 K appears to have no known counterpart in molecular organometallic compounds.

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References

1 K. Nakamoto, 'Infrared and Raman Spectra of Inorganic and Coordination Compounds,' 3rd edn., Wiley-Interscience, New York, 1977.

2 B. E. Koel, J. E. Crowell, C. M. Mate, and C. A. Somorjai, *J. Phys. Chem.*, 1984, **88**, 1988.

3 N. R. Avery, *Surf. Sci.*, 1984, **146**, 363.

4 C. M. Friend and E. L. Muetterties, *J. Am. Chem. Soc.*, 1981, **103**, 773.

5 Min-Chi Tsai and E. L. Muetterties, *J. Phys. Chem.*, 1982, **86**, 5067.

6 Min-Chi Tsai and E. L. Muetterties, *J. Am. Chem. Soc.*, 1982, **104**, 2534.

7 N. R. Avery and N. Sheppard, *Proc. Roy. Soc. London, Ser. A*, 1986, **405**, 1, 26.