

Low Temperature Catalytic Chemistry of the Pd(111) Surface: Benzene and Ethylene from Acetylene

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Acetylene reacts to form benzene on Pd(111) at *ca.* 200 K; photoelectron spectroscopy indicates that the reaction intermediate lies flat, and that competitive formation of ethylene involves an intermediate with perpendicular adsorption geometry.

The homogeneously catalysed reaction of acetylene to yield benzene at room temperature is a well known process for transition metal cluster compounds,¹ whereas heterogeneously catalysed aromatisation reactions are usually encountered only at much higher temperatures on bifunctional catalysts (*e.g.*, ref. 2, *ca.* 550 K on Pt-SiO₂). Recently, however, Bertolini *et al.*³ have observed benzene formation from acetylene over Ni-SiO₂ at 300 K. This communication reports on the first observation of a low temperature (*ca.* 200 K) heterogeneously catalysed reaction of acetylene to form benzene on a *pure Pd(111) single crystal* surface in a well controlled environment.

Matheson research grade acetylene was further purified by six bulb-to-bulb distillations and dosed onto the atomically clean Pd(111) surface at *ca.* 175 K by means of a molecular beam. The structure and composition of the clean surface and the various adsorbed phases were characterised by low energy electron diffraction, Auger and X-ray photoelectron spectroscopy, and by angle-resolved u.v. photoelectron (u.p.) spectroscopy. Experimental details have been described elsewhere.⁴ On raising the specimen temperature at 20 K s⁻¹ desorption products could be detected and identified by mass spectrometry. Figure 1 shows such temperature programmed reaction spectra for hydrogen, ethylene, and acetylene (2, 28 and 26 a.m.u.,

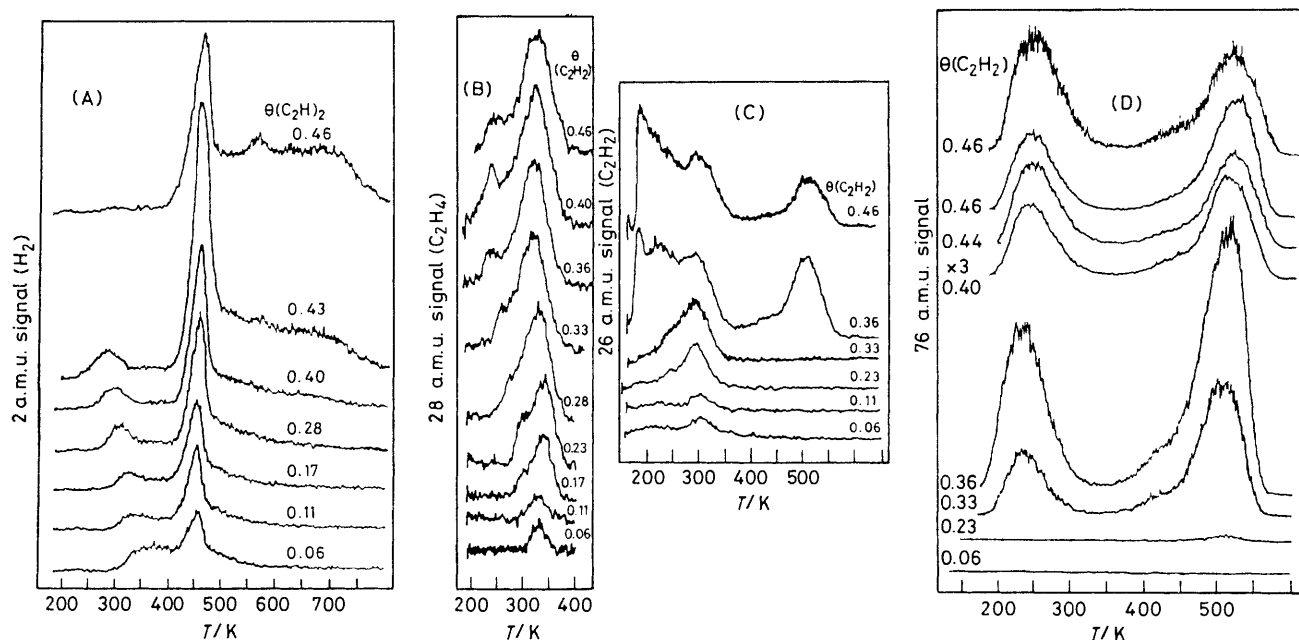
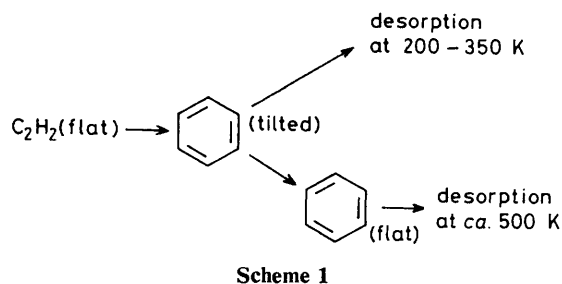
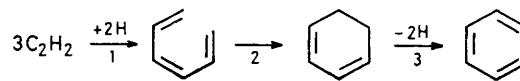


Figure 1. Temperature programmed reaction spectra showing desorption of H_2 (A), C_2H_4 (B), C_2H_2 (C), and C_6H_6 (D) for various initial fractional coverages of acetylene θ (C_2H_2). Dosing temperature 175 K.



Scheme 1



Scheme 2

respectively); also shown are 78 a.m.u. spectra which are exactly mirrored by 51 a.m.u. spectra (not shown). These latter signals correspond to high abundance ions in the mass spectrum of benzene. The identification of benzene as a reaction product was confirmed by measuring the intensity of a number of fragment ions peaks which coincided with the peaks in the 51 and 78 a.m.u. spectra. Specifically, the relative intensities at 78, 77, 76, 75, 51, and 50 a.m.u. were in excellent agreement with the mass spectrum of benzene measured in the same apparatus.

U.p. spectra were measured for the adsorbed layer at *ca.* 160 K for normal electron exit and as a function of angle of incidence of the unpolarised photon beam ($h\nu = 21.2$ eV). The results indicated that this phase consisted of 'flat-lying' acetylene-like species (*i.e.* $C\equiv C$ parallel to the Pd surface); a surface which was dosed with acetylene at *room temperature* exhibited features ascribable to benzene orbitals.⁵ The indications are that these initially formed benzene molecules are tilted with respect to the surface plane (loss of C_{6v} symmetry). Control experiments showed that chemisorption of benzene itself resulted only in a *high temperature* desorption peak at 510 K. identical to that in Figure 1 which of course refers to reactively formed benzene.

The mechanism shown in Scheme 1 accounts for these observations. Support for this mechanism derives from the

u.p.s.⁴ observation that benzene chemisorption on Pd(111) *does* result in a flat-lying species (C_{6v}). Thus low temperature benzene evolution would appear to be associated with a tilted molecule formed on an initially crowded surface. As the surface becomes depleted of reactant and product molecules, some of these species can adopt the flat configuration (more strongly chemisorbed), eventually desorbing at *ca.* 500 K. The observation of ethylene as a product suggests that partial hydrogenation of acetylene is competitive with cyclisation. This is confirmed by pre-dosing the surface with H_2 ; benzene formation is almost completely suppressed and ethylene production correspondingly enhanced. The angle-resolved u.p. spectra suggest that the intermediate to ethylene formation is a vinylidene-like species ($=C=CH_2$) with the C–C axis *perpendicular* to the metal surface.

The mechanism of the low temperature cyclisation may involve initial formation of hexa-1,3,5-triene which then undergoes closure to cyclohexadiene (a reaction which proceeds easily at low temperatures and in the absence of catalysts).⁶ This could be followed by Pd-induced dehydrogenation and eventual desorption of benzene (Scheme 2).

Step 2 of this speculative mechanism provides a basis for understanding why the initially formed benzene might be tilted with respect to the surface. It is also consistent with the known structure and reactive properties of C_6 alkyne-bridged clusters of, for example, molybdenum and cobalt.⁷ A further point of interest is that $Os_3H_2(CO)_6C_6H_4$ has recently been shown⁸ to contain a benzene molecule in which the ring is tilted at 70° with respect to the plane of metal atoms.

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