



# 1,2-Dichloroethene on Cu(1 1 0): Adsorption, dechlorination and trimerisation reactions

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This paper is dedicated by the authors to the memory of Eric Derouane, formerly Director of the Leverhulme Centre for Innovative Catalysis, University of Liverpool, whose leadership, encouragement and energy inspired this and many other valuable and continuing academic-industrial research collaborations.

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Dichloroethene  
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## ABSTRACT

The adsorption and reactions of *cis*-1,2-dichloroethene on Cu(1 1 0) have been investigated using Reflection Absorption Infrared Spectroscopy, Temperature Programmed Desorption and Molecular Beam Adsorption Reaction Spectroscopy, and the behaviour compared with that of the previously studied [S. Haq, S.C. Laroze, C. Mitchell, N. Winterton, R. Raval, Surf. Sci. 531 (2003) 145] *trans* isomer. No isomerisation between the *cis* and *trans* isomers was seen. The data reveal that, although the related positions of the Cl atoms force different adsorption geometries for the two isomers, the behaviour of both compounds follows a very similar general reaction pathway which is critically temperature-dependent and can be described in terms of three main regimes: Regime I occurring at low temperatures in which intact molecular adsorption occurs; Regime II, extending over the temperature range of 155–280 K, in which desorption/dechlorination events are triggered; and, finally, Regime III, over 280–450 K, is governed, for both isomers, by the behaviour of the acetylene intermediate at the surface which trimerises to form benzene and desorbs above 350 K.

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## 1. Introduction

Chlorinated organic compounds are industrially important both in their own right and as feedstocks or intermediates [1], though the poor selectivity of some processes leads to unwanted by-products. Industry therefore has sought improved processes that respond to changes in demand and the need to minimise waste by effecting more selective transformations and consuming by-products as feedstocks. For these reasons, hydrodechlorination, the conversion  $C-Cl + H_2 \rightarrow C-H + HCl$ , represents a reaction of industrial and technological importance. Group VIII(8–10) metals, particularly palladium, platinum and copper, appear to be the most attractive hydrodechlorination catalysts in terms of activity, selec-

tivity and stability [4,5]. Fundamental studies [2,3,6–26] on well defined single crystal surfaces and UHV conditions using surface spectroscopic techniques are aiding our understanding of the interactions of chlorinated compounds with the surfaces of these metals, enabling insights to be gained into mechanistic changes associated with the metal, surface structure, temperature, coverage and the molecular structure of the chlorinated compound.

The study of dichloroethenes (DCEs) enables the behaviour of simple unsaturated chlorinated species with metal surfaces to be delineated and, in particular, the reactivity patterns of different isomers to be contrasted. Previous work has studied the adsorption and reaction of chloroethenes on Pt(1 1 1) [17], Pt(1 0 0) [17], Pd(1 1 0) [13], Cu(1 0 0) [18] and Cu(1 1 0) [2,11]. In this paper [3], the adsorption, reactive transformation and product evolution of *cis*-1,2-dichloroethene on Cu(1 1 0) are reported and compared particularly with related studies on the *trans* isomer [2], continuing efforts to characterise and understand the interactions of a series of chlorinated ethenes with well-defined metal surfaces, including Cu(1 1 0) [2,11,12], Pd(1 1 0) [13] and CuPd(1 1 0) [14–16] and Cu nanoparticles [24,25].

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## 2. Experimental

The experimental details of the characterisation methods and equipment used to carry out Molecular Beam Adsorption Reaction Spectroscopy (MBARS), Reflection Absorption Infrared Spectroscopy (RAIRS), Low Energy Electron Diffraction (LEED), Auger Electron Spectroscopy (AES) and Temperature Programmed Desorption (TPD), have been described in detail previously [2]. The experiments were performed in a ultra-high vacuum (UHV) chamber and the Cu(110) crystal was cleaned by sputtering (500 eV, 8  $\mu$ A), annealed at ca. 873 K and characterised using LEED and AES. TPD experiments were carried out using a heating rate of 2 K s<sup>-1</sup>. For RAIRS measurements the UHV chamber is interfaced with a FTIR spectrometer (Mattson-Galaxy) using KBr optics. A liquid nitrogen cooled mercury–cadmium–telluride (MCT) detector was used, accessing the spectral range of 4000–650 cm<sup>-1</sup>. Spectra were acquired at a resolution of 4 cm<sup>-1</sup> and by co-addition of 256 scans. The liquid *cis*-1,2-dichloroethene sample (Supelco, 99% purity) was subjected to freeze-pump-thaw cycles prior to admission into the chamber and the purity of each sample was confirmed using mass spectrometry. The exposures are quoted in Langmuirs (L) where 1L = 1  $\times$  10<sup>-6</sup> Torr s.

## 3. Results and discussion

Our previous work on *trans*-dichloroethene on Cu(110) [2,11] and Pd(110) [13] clearly demonstrates that the reaction of this molecule occupies a complex phase space, with five different reaction regimes identified for Pd(110) and three on Cu(110). Here, we show that the behaviour of the *cis* isomer is broadly similar to the *trans*-isomer on Cu(110).

The adsorption of *cis*-1,2-dichloroethene on Cu(110) was followed as a function of exposure over the temperature range of 85–450 K. RAIRS was used to obtain chemical and molecular information on the adlayer while TPD and MBARS were utilised to detect the evolution of products. From these data, reaction regimes I–III can be identified, as shown in the TPD events following 14 L exposure of *cis*-1,2-dichloroethene to Cu(110) at 83 K (Fig. 1). Regime I,

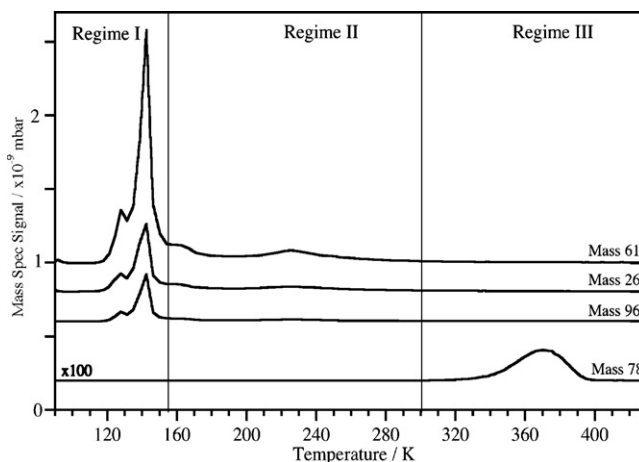


Fig. 1. TPD spectra after adsorption of 14 L *cis*-1,2-dichloroethene on Cu{110} at 85 K. The main reactivity regimes shown by this system are marked.

occurring between 85 and 155 K, characterises molecular adsorption in the monolayer and the multilayer. In Regime II, the retained monolayer undergoes desorption/dechlorination processes; and finally, in Regime III (280–450 K), the reaction of the acetylene intermediate dominates the system behaviour. Each of these reaction regimes is described in more detail below.

### 3.1. REGIME I: non-dissociative molecular adsorption; 85–155 K

The RAIR spectra obtained after 0.75–8.75 L exposure of *cis*-1,2-dichloroethene at 85 K (Fig. 2A) display a continuous increase in the intensity of all IR bands, with the highest exposure corresponding to an adsorbed multilayer. The infrared spectrum of the multilayer is similar to that reported for *cis*-1,2-dichloroethene in the gas and liquid phase [27–30], with bands at 715, 848, 1292, 1589 and 3081 cm<sup>-1</sup> due to fundamental modes of vibrations (Table 1). The orientation of *cis*-DCE in the multilayer may be deduced by applying the dipole selection rule to a metal surface [21]. In partic-

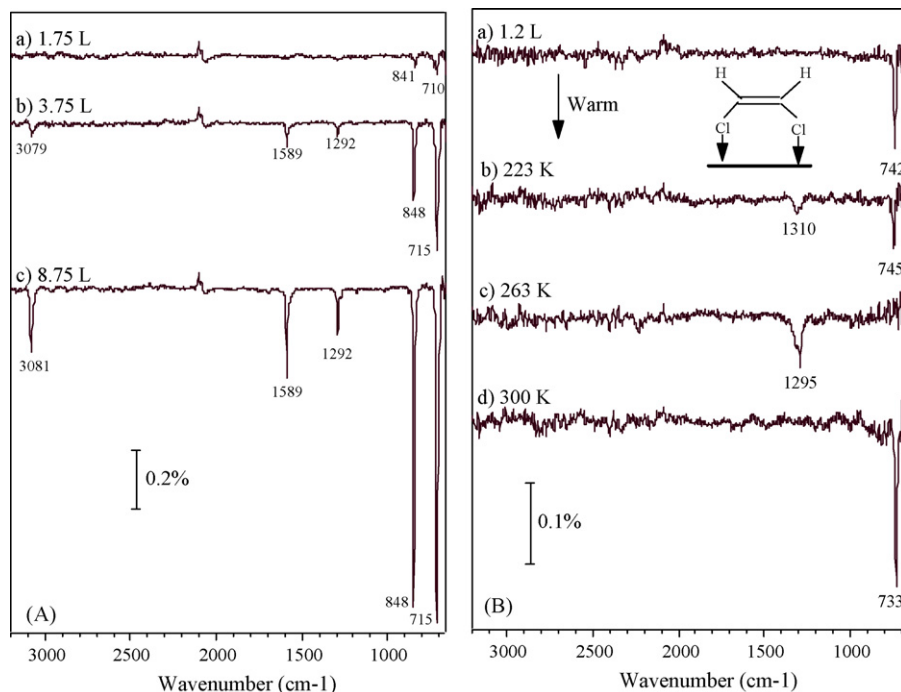


Fig. 2. RAIR spectra following (A) increasing exposure of *cis*-1,2-dichloroethene on Cu{110} at 85 K, (B) adsorption of 1.2 L at 177 K and the effect of heating.

**Table 1**

Assignment of vibrational frequencies observed in this work and those listed in Ref. [28].

Assignment in the liquid/gas phase	Normal mode description	Liquid/gas phase frequency	Observed on Cu{1 1 0}multilayer
$\nu_1$ ( $A_1$ )	$\nu_s$ (C–H)	3077 (IR, R) vs	
$\nu_2$ ( $A_1$ )	$\nu$ (C=C)	1590 (IR, R) s	1589
$\nu_3$ ( $A_1$ )	$\delta$ (C–H)	1183 (IR, R) s	1179
$\nu_4$ ( $A_1$ )	$\nu_s$ (C–Cl)	714 (IR, R) s	715
$\nu_5$ ( $A_1$ )	$\delta$ (C=C)	173 (IR, R) s	
$\nu_6$ ( $A_2$ )	$\tau$ (HCIC=CCH)	876 (R)	
$\nu_7$ ( $A_2$ )	$\gamma$ (C–Cl/H)	406 (R)	
$\nu_8$ ( $B_1$ )	$\nu_{as}$ (C–H)	3072 (IR) s	3081
$\nu_9$ ( $B_1$ )	$\delta$ (C–H)	1294 (IR) s	1292
$\nu_{10}$ ( $B_1$ )	$\nu_{as}$ (C–Cl)	848 (IR) vs	848
$\nu_{11}$ ( $B_1$ )	$\delta$ (C–Cl)	571 (IR) s	
$\nu_{12}$ ( $B_2$ )	$\gamma$ (C–H)	697 (IR) vs	

IR = infra-red; R = Raman; vs = very strong; s = strong.

ular we point out the almost equal intensities of the  $B_1$  asymmetric  $\nu_{as}$ C–Cl stretch and the  $A_1$  symmetric  $\nu_s$ C–Cl stretch at 848 and 715  $\text{cm}^{-1}$ , respectively, suggests that the molecular plane and the C=C bond are, on average, highly tilted away from the surface plane. This behaviour is different from that observed for *trans*-DCE which shows a strong preference for adopting an orientation in which the molecular plane and the C=C bond are held parallel to the surface. Clearly, the relative positioning of the Cl atoms leads to a very significant difference in packing. However this packing difference does not affect the desorption temperature of the *cis*-1,2,DCE multilayer which occurs at 142 K, Fig. 1, and is identical to *trans*-DCE within experimental error.

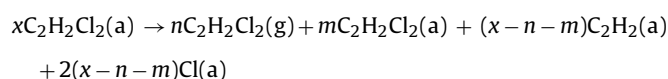
### 3.2. REGIME II: desorption limited dechlorination events in the monolayer; 155–280 K

Upon heating to 177 K, desorption of the weakly held multilayer occurs, leaving a more strongly adsorbed monolayer at 177 K. Fig. 2B shows that the RAIRS spectrum obtained for this adlayer is quite different from that of the multilayer, displaying a single strong absorbance at 742  $\text{cm}^{-1}$ . We attribute this band to the  $A_1$  symmetric  $\nu_s$ C–Cl stretch and suggest that the upshift in frequency from the gas phase value arises as a result of direct interaction between the Cl atoms on the molecule and the Cu atoms in the surface. This behaviour is consistent with density functional theory (DFT) calculations carried out on trichloroethene on CuPd(110) [6] where the surface interaction is dominated by Cl–Cu bonding and leads to a strong perturbation of the C–Cl bond. It is proposed that in order to maximise this interaction, the *cis*-1,2-DCE orients itself with the C=C bond parallel but the molecular plane normal to the surface allowing both Cl atoms to interact directly. Such an adsorption geometry would also explain why the  $A_1$  symmetric  $\nu_s$ C–Cl stretch is observed but not the  $B_1$  asymmetric  $\nu_{as}$ C–Cl stretch. This appears to be an activated process as this adsorption symmetry is not observed at 85 K.

Upon increasing temperature to 223 and 263 K, changes are observed in the RAIRS spectra, with the molecular band at 745  $\text{cm}^{-1}$  decreasing rapidly so that it is no longer visible at the latter temperature, accompanied by growth of a new band at  $\sim 1295 \text{ cm}^{-1}$ . On the basis of our previous studies of *trans*-DCE on Cu(1 1 0) [2] and using the fingerprint analysis of Sheppard [31,32], we assign this band to the  $\nu$ (C=C) stretch of a di- $\sigma$ /di- $\pi$  acetylene intermediate arising from dechlorination of the molecule. We also note that the vibrational literature reported for  $\text{C}_2\text{H}_2$  adsorbed on Cu single crystal surface all show a significant 1292  $\text{cm}^{-1}$  peak [31–36]. From the TPD data, Fig. 1, it can be seen that the changes in the RAIRS spectra coincide with a broad molecular desorption peak in this temperature range. This suggests that the observed dechlorination is desorption-limited, *i.e.* vacant surface sites to be released to accommodate the products of a surface reaction. No desorption

of chlorine is seen in this temperature range, suggesting that it is still attached to the copper surface.

Regime II thus comprises of the overall following process:



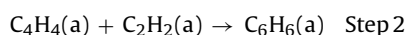
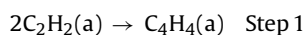
### 3.3. REGIME III: reactions of molecular intermediates; 280–450 K

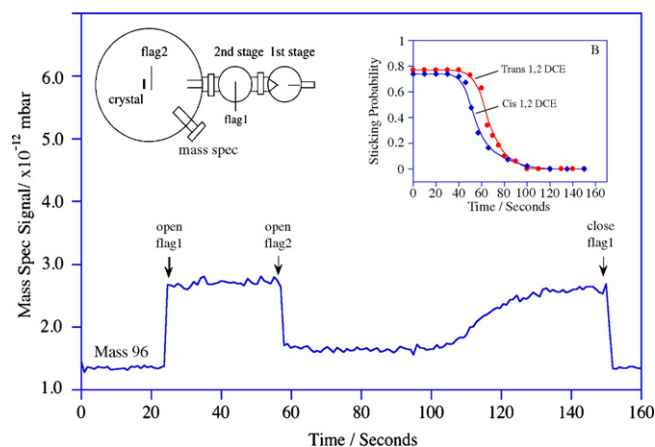
Regime III is dominated by the reactions of the surface-bound molecular intermediates and was investigated using structural spectroscopic studies, TPD and thermal molecular beam experiments.

#### 3.3.1. Structural studies of the adsorbed layer

RAIRS data show that at 300 K, a new species is created at the surface, producing a single dominant band at 733  $\text{cm}^{-1}$ , Fig. 2B, closely resembling the out-of-plane  $\gamma$ (C–H) bending mode observed for benzene on Cu(1 1 0) [37]. This is the major dipole-allowed mode of a flat-lying benzene species, also seen at the same position in related experiments using *trans*-DCE on Cu(1 1 0), suggesting that a trimerisation reaction of the adsorbed acetylene has occurred. The frequency of the out-of-plane  $\gamma$ C–H mode is upshifted compared to the gas-phase molecule (671  $\text{cm}^{-1}$ ) or to adsorbed benzene on clean Cu(1 1 0) [37] where it occurs at 685  $\text{cm}^{-1}$ . This increased frequency has been directly attributed to a stronger interaction of benzene [38] with a Cl-covered surface where the electrostatic field of the halogen increases the local work-function, inducing an increase in charge donation from benzene to Cu. TPD data, Fig. 1, directly support this by showing that benzene is evolved at a temperature of 370 K when mass 78 ( $\text{C}_6\text{H}_6$ ) and the known benzene fragments at amu 50, 51 and 52 desorb simultaneously although they are not shown. In contrast, benzene adsorption is limited to <300 K on clean Cu(1 1 0) [37] and Cu(1 1 1) [39]. We conclude from the increased strength of benzene chemisorption that product formation from cyclotrimerisation is desorption-limited on Cl-contaminated Cu(1 1 0), whereas it is reaction-limited on clean Cu(1 1 0) [33,40]. Other possible desorption products, such as hydrogen, hydrogen chloride or carbon-containing compounds, are not seen.

The mechanism of trimerisation of acetylene on extended surfaces is thought to be similar to that observed in homogeneous catalysis using transition-metal cluster compounds. A stepwise mechanism, shown below is thought to occur:





**Fig. 3.** Schematic of molecular beam apparatus and procedure used. The inset shows comparison of  $S_0$  against temperature for *cis*- and *trans*-1,2-dichloroethene.

We were unable to observe the metallopentacycle species in the IR spectra but the data in our studies of *cis*- and *trans*-DCE are in agreement with the general mechanism shown above, with Step 1 appearing to be the rate determining step for benzene formation.

### 3.3.2. Molecular beam studies

Using molecular beam studies to monitor reactive adsorption as a function of temperature provides valuable information about sticking coefficients and general adsorption kinetics. Fig. 3 illustrates the apparatus and procedure used and the typical uptake profile obtained for adsorption of *cis*-1,2-dichloroethene at 296 K. The beam enters the analysis chamber on opening flag 1 and is totally reflected from the inert flag 2 in front of the crystal. When this second flag is removed the beam strikes the crystal and the signal decreases as adsorption proceeds. Once the surface is saturated the signal recovers back to the level observed from reflection off flag 2.

Sticking probability curves obtained from such MBARS data are shown for both the *trans* and the *cis* isomer collected at 296 K. Within experimental error and variation of beam flux between the two experiments, it can be concluded that both isomers show very similar behaviour, namely that the initial sticking probability,  $S_0$ , is high at  $\sim 0.75$ , and the shape of the  $S$  versus time curve is indicative of precursor adsorption kinetics.

## 4. Conclusions

The adsorption and reaction behaviour of *cis*-1,2-dichloroethene on Cu(110), studied over the temperature range 85–450 K, shows that the reaction of this molecule follows a reaction pathway that is broadly similar to that exhibited by *trans*-1,2-dichloroethene on Cu(110). In both cases, the reaction phase space can be divided into three regimes where different events occur: Regime I (85–155 K) representing molecular adsorption in the monolayer and the multilayer; Regime II (155–280 K) in which desorption and dechlorination occur to leave acetylene and coadsorbed Cl atoms at the surface; and, Regime III (280–450 K) where acetylene trimerises to benzene, which subsequently desorbs. Overall, copper is found to be extremely effective at cleaving the C–Cl bond (observed as

low as 220 K in our work), while the C–H bond remains intact. In this respect, the behaviour of Cu differs significantly from group VIII metals such as Pd(110) [13] where the ease of C–H bond fission leads to the dominance of HCl or H<sub>2</sub> production in much of the reaction phase diagram.

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