

## An E.S.C.A. Study of the Dissociative and Associative Chemisorption of Halogeno-alkenes and -alkynes on a Pt(100) Surface

By TERENCE A. CLARKE, IAN D. GAY, and RONALD MASON\*

(School of Molecular Sciences, University of Sussex, Brighton BN1 9QJ)

*Summary* Quantitative u.h.v.-e.s.c.a. studies of the chemisorption of  $F_3C-C\equiv CH$ ,  $H_2C=CHF$ ,  $H_2C=CF_2$ , *cis*- $FHC=CHF$ , and  $F_2C=CFCl$  on a clean Pt(100) surface show that the initial sorption of vinyl fluoride and 1,1-

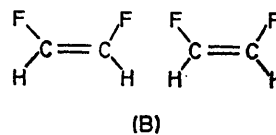
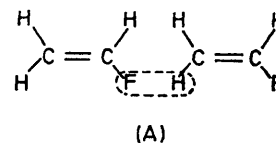
difluoroethylene is dissociative, the chemisorption of trifluoropropyne, *cis*-1,2-difluoroethylene, and trifluorochloroethylene being associative; a mechanism for the dissociation reaction is suggested.

AN Auger electron spectroscopic study<sup>1</sup> of the chemisorption of vinyl fluoride and vinyl chloride on a clean Pt(100) surface suggested that their adsorption was largely dissociative; no fluorine KVV Auger transition was observed, for instance, during the chemisorption of vinyl fluoride and hexafluoropropene. The addition of e.s.c.a. facilities to our u.h.v.-mass spectrometry, Auger, i.e.e.d. combination instrument has now provided spectroscopic observations which allow a more complete interpretation of the events accompanying the adsorption of substituted alkenes and alkynes.

The essential results, derived from Al- $K_{\alpha}$  (1486.6 eV) photoelectron spectroscopy of the ligand binding energies and integrated transition intensities at various coverages of the platinum surface, are collected in the Table.

Up to monolayer coverage, with effective zero escape depth, the photoelectron peak intensities and energies of non-dissociatively chemisorbed molecules should be very similar to the spectra of these molecules in the gas phase. This assertion is borne out by the observations on trifluoropropene and carbon monoxide. For the alkyne, the two

studies of chemisorption show that Auger spectroscopy has little value, following universal electron beam-induced fragmentation and/or desorption. The exposure ( $\geq 30L$ )



of the platinum surface to vinyl fluoride in excess of approximately one third saturation coverage [e.s.c.a. C(1s) integr-

TABLE. Chemisorption on platinum: ligand binding energies and integrated e.s.c.a. intensities

Ligand	Ligand atoms binding energies (eV) referred to Pt(4f <sub>7/2</sub> ) = 71.1 eV <sup>a</sup>	Exposure (Langmuir)	Integrated C(1s) peak intensity	Integrated 'other atom' peak intensity <sup>b</sup>	R(F/C) (expt.)	R(F/C) (theor.) <sup>c</sup>	
F <sub>3</sub> C'-C≡CH	C(1s) = 284.1(3)	100	10.2(4)	74.0(6)	15.1	13.7	
	C'(1s) = 291.3(3)		4.9(4)				
H <sub>2</sub> C=CHF	F(1s) = 686.5(3)	15	3.1(4)	1.0(2)	0.3	2.27	
	C(1s) = 284.6(3)		3.7(4)	3.1(3)	0.9		
	F(1s) = 685.6(3)		4.2(4)	5.6(3)	1.3		
			100	5.8(4)	8.0(4)		1.4
			200	6.7(5)	8.0(4)		1.2
H <sub>2</sub> C=CF <sub>2</sub>	C(1s) = 285.2(5)	30	0.8(2)	2.1(2)	2.7	4.55	
	(small diffuse peak)		1.4(2)	4.3(3)	3.1		
	F(1s) = 685.7(5)		200	1.8(2)	5.4(3)		3.0
<i>cis</i> -FHC=CHF	C(1s) = 285.7(3)	100	7.6(3)	35.3(5)	4.6	4.55	
	F(1s) = 685.6(5)						
F <sub>2</sub> C=CFCl	C(1s) = 286.7(3)	200	5.0(3)	32.5(5)	6.5	6.8	
	F(1s) = 685.6(5)			Cl = 3.9(2)			
	Cl(2p) = 199.0(3)						
H <sub>2</sub> C=CH <sub>2</sub>	C(1s) = 284.3(3)	100	10.0(4)	—	—	—	
CO	C(1s) = 286.6(3)	100	6.7(3)	O = 19.9(4)	R(O/C) = 3.0	R(O/C) = 2.9	
	O(1s) = 532.0(4)						

<sup>a</sup> Ref. 2. <sup>b</sup> The chlorine, fluorine, and oxygen intensities have been corrected for the dependence of the analyser sensitivity on the kinetic energies of the electrons;<sup>3</sup> variations in the multiplier gain have been corrected by continuous reference to the Pt(4f<sub>3/2</sub>) emission from the clean surface. <sup>c</sup> Calculated from theoretical ionisation cross-sections.<sup>4</sup>

C(1s) peaks are separated by 7.2 eV which should be compared with the 8.3 eV separation of the carbon 1s binding energies in methane and fluoroform;<sup>5</sup> their relative intensities are 2.1(2) (the figures in parentheses are the e.s.d.s of the accompanying observation, referred to the least significant digit) and, more important for our present argument, the fluorine-carbon intensity ratio is identical within experimental error, to the ionisation cross-section ratio.<sup>4</sup> A similar result is obvious for carbon monoxide on platinum and has been observed also for its chemisorption on polycrystalline tungsten.<sup>6</sup>

The data for vinyl fluoride show that initial chemisorption is dominated by dissociative events involving the loss of fluorine from the surface. Parenthetically, we note that the Auger experiments<sup>1</sup> must be interpreted in terms of desorption of the fluorine by the electron beam; all our

ated intensity] gives largely associatively adsorbed species, the observed fluorine-carbon ratio then approaching the theoretical value. Adsorption data for vinyl chloride are very similar.

Both 1,1-difluoroethylene and trifluorochloroethylene have low sticking probabilities (*ca.*  $2 \times 10^{-3}$  and  $5 \times 10^{-3}$  respectively) but sufficiently quantitative data can be obtained to demonstrate the dissociative adsorption of F<sub>2</sub>C=CH<sub>2</sub> and the nondissociative sorption of F<sub>2</sub>C=CFCl. The obvious implication is that the initial adsorption of the vinyl halides and of 1,1-difluoroethylene proceeds *via* the elimination of HF or HCl and two possibilities, both based on an initial oxidative addition of the metal to a C-H bond rather than cleavage of a C-X bond, need to be discussed.

An intramolecular elimination of HX seems unlikely in view of the nondissociative chemisorption of 1,1-dichloro-

ethylene—in contrast to its difluoro-analogue. So far as elimination of HX from neighbouring molecules on the surface is concerned, we note that, like ethylene,<sup>1</sup> substituted alkenes and alkynes have a diffuse C(2×2) structure for the Pt(100)-ligand surface. The centres of translationally equivalent ligands are 5.6 Å apart and with an ordered 'head to tail' packing (A), the intermolecular H···F distance is *ca.* 2.5 Å. An identical situation is obvious for 1,1-difluoroethylene but may be excluded for 1,1-dichloroethylene by the larger van der Waals diameter of chlorine. For the *cis*-1,2-difluoroethylene, ordering of the kind (B) would not allow ready HF elimination since the lateral non-bonded H···F distances are now larger.

Quantitative intensities from e.s.c.a. studies of chemi-

sorbed ligand states can clearly provide data on the nature of surface species which are not accessible by other methods. Elsewhere, we discuss<sup>7</sup> complementary results on the modification of the platinum valence band structure following chemisorption. It is not obvious, however, at present why significant dissociation occurs only up to approximately one-third monolayer coverage and whether it takes place at defect or other electron-rich sites; some valuable data may be forthcoming from experiments on stepped surfaces.

We are grateful to the S.R.C. for support of these studies and to Simon Fraser University for sabbatical leave (I.D.G.).

(Received, 15th February 1974; Com. 201.)

<sup>1</sup> T. A. Clarke, R. Mason, and M. Tescari, *Proc. Roy. Soc.*, 1972, *A*, **331**, 321.

<sup>2</sup> J. A. Bearden and A. F. Burr, *Rev. Mod. Phys.*, 1967, **39**, 128.

<sup>3</sup> ESCA 3 Operating Manual, 1972, Vacuum Generators Ltd.

<sup>4</sup> C. D. Wagner, *Analyt. Chem.*, 1972, **44**, 1050; B. L. Henke and R. L. Elgin, *Adv. X-ray Anal.*, 1970, **13**, 639.

<sup>5</sup> T. D. Thomas, *J. Amer. Chem. Soc.*, 1970, **92**, 4184.

<sup>6</sup> T. E. Madey, J. T. Yates, Jr., and N. E. Erickson, *Chem. Phys. Letters*, 1973, **19**, 487.

<sup>7</sup> T. A. Clarke, I. D. Gay, and R. Mason, in preparation.