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ELECTROCHEMICAL OXIDATION OF ADSORBED ALKENOIC ACIDS AS A FUNCTION OF CHAIN LENGTH AT Pt(111) ELECTRODES. STUDIES BY CYCLIC VOLTAMMETRY, EELS AND AUGER SPECTROSCOPY

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Studies of the electrochemical oxidation of a series of straight-chain terminal alkenoic acids adsorbed at a Pt(111) electrode surface are reported. Compounds adsorbed were: propenoic acid (acrylic acid, PPA); 3-butenoic acid (vinylacetic acid, 3BTA); 4-pentenoic acid (allylacetic acid, 4PTA); 6-heptenoic acid (6HPA); and 10-undecenoic acid (10UDA). Vibrational spectra of adsorbed layers were obtained by use of electron energy-loss spectroscopy (EELS). Molecular packing densities were measured by use of Auger spectroscopy. Electrochemical oxidation of each adsorbed layer was explored by means of cyclic voltammetry in aqueous inert electrolyte (KF/HF). As the analogous aliphatic acids are not chemisorbed at Pt under the same conditions, the alkenoic acids evidently adsorb at Pt(111) predominantly through the C=C double bond. Molecular packing densities indicate that the carboxylic acid moiety is in contact with the Pt surface only in the case of PPA. EELS spectra also indicate that the carboxylate groups (other than in PPA) are present as pendants. The carboxylic acid O–H stretching bands of most of the adsorbed acids are red-shifted and broadened, evidently due to extensive intermolecular hydrogen bonding; the exceptions are PPA, for which the interaction is primarily with the Pt surface, and 3BTA, for which intermolecular interaction between the carboxylic acid pendants is apparently prevented by steric considerations. The surface-attached carboxylic acid moieties react with KOH solution, leading to retention of K^+ ions, detected by Auger spectroscopy, and to changes in the vibrational spectra indicative of carboxylate anions; reactivity toward KOH decreases with chain length. Adsorbed alkenoic acids at Pt(111) surfaces are stable in water and in vacuum. Oxidation of the adsorbed short-chain acids PPA and 3BTA proceeds to completion, forming CO_2 as the principal product. Oxidation of the adsorbed long-chain acids converts the C=C moiety to $2CO_2$, and transforms the remainder of the molecule to an unadsorbed diacid (likely possibilities are malonic acid from 4PTA; glutaric acid from 6HPA; and heptane-1,7-dioic acid from 10UDA).

Electrochemical oxidation, alkenoic acids on platinum.

1. Introduction

Chemical compounds belonging to a wide variety of classes are being studied at well-defined electrode surfaces with respect to the nature of species which are

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adsorbed from solution, vapor or pure liquid, and with regard to the types of chemical reactions undergone by adsorbed layers of those compounds [1]. The types of compounds studied thus far include aromatic diphenols [2a], hydroxy-biphenyls [2b], mercaptans [2c], amino acids [2d], unsaturated alcohols [2e,f], pyridines and pyridine carboxylic acids such as niacin [2g], bipyridyls [2h], biphenyls [2h], phenylpyridines [2h], and multi-nitrogen heteroaromatics [2i]. Ionic adsorbates [2j–o] and electrodeposited metallic layers [2o–r] are also being investigated. Substrates studied include Pt(111) [1], Ag(111) [2r–s], FeCrNi alloy(111) [2t–u], Pt(1000) [2v] and Pt(s)[6(111) × (111)] [2w].

Adsorbate vibrational states and modes of surface attachment are explored by use of electron energy-loss spectroscopy (EELS) [3]. Molecular packing densities and elemental compositions are determined by Auger electron spectroscopy (AES) [2x]. Long-range surface order is confirmed by low-energy electron diffraction (LEED) [2y], as those processes are extremely sensitive to electrode surfaces structure. Electrochemical reactivity is investigated by cyclic voltammetry and chronocoulometry [2y–z]. UHV spectroscopic characterization and aqueous electrochemistry of organic adsorbates are accomplished by means of a specially constructed surface electrochemistry apparatus which eliminates possible contamination of the surface which could occur if the surface were allowed contact with air [1]. Previous studies have explored the nature of various chemisorbed species, including elemental composition, molecular constitution, orientation, mode of attachment to the surface, molecular packing density, stability of surface bonding towards solution and vacuum, influence of surface structure on bonding, spectra, and catalytic activity and the electrochemical reactivity of the adsorbed species. Results have demonstrated that atoms, ions, or molecules chemisorbed from solution are quite stable in vacuum and can therefore be characterized in detail by electron spectroscopic methods.

The present investigation involves surface spectroscopic characterization and electrochemical oxidation of straight-chain, terminal alkenoic acids, varying in chain length from three to eleven carbons adsorbed at Pt(111) electrodes. We are not aware of any previous LEED/Auger/EELS/voltammetry studies of adsorbed alkenoic acids. EELS, Auger spectroscopy and voltammetry indicate that the alkenoic acids are attached to Pt(111) primarily through the C=C double bond. The carboxylic acid moieties are pendant and intermolecularly hydrogen bonded, with the exception of short-chain compounds such as propenoic and 3-butenoic acid. Electrochemical oxidation of propenoic and 3-butenoic acid goes to completion, producing CO_2, while oxidation of the longer-chain terminal alkenoic acids converts only the unsaturated carbons to CO_2 and desorbs the remainder of the molecule in the form of a dicarboxylic acid. Analogous oxidation behavior is observed with the terminal alkenols [2e]. Oxidation of the Pt surface hinders further adsorption of alkenes (2z).

2. Experimental

Experimental procedures employed for this work were as described previously [1]. Specially constructed instrumentation utilized for these studies permits study of adsorbed layers at well-defined surfaces by vibrational spectroscopy (electron energy-loss spectroscopy, EELS), Auger electron spectroscopy, low-energy electron diffraction (LEED) and electrochemical techniques (coulometry and cyclic voltammetry at ambient argon pressures in an adjoining antechamber).

The Pt(111) single crystal employed for these studies was oriented and polished such that all six faces were crystallographically equivalent to the (111) plane. All six faces were cleaned simultaneously by bombardment with Ar^+ ions and annealed by resistance heating (about 1000 K) in ultrahigh vacuum. After characterization, the clean, annealed Pt(111) surface was isolated in an argon-filled antechamber and immersed into various electrolytic solutions of alkenoic acids to adsorb the acids. Electrode potentials and currents were measured and controlled by means of standard electrochemical circuitry based upon operational amplifiers. Potentials were referred to a standard Ag/AgCl reference electrode prepared with 1.0 M KCl. The electrochemical cell, reference half-cell and Pt auxiliary electrode were contained in a Pyrex glass cell and solutions introduced through Teflon jacketed tubing. The jacket was continuously purged with argon to minimize diffusion of air through tubing walls in contact with the solutions. The cell assembly was introduced into the argon-filled antechamber by means of a bellows and gate valve. Solutions employed for the adsorption of the subject alkenoic acids contained 10 mM KF (Puratronic Grade, Johnson Matthey, Inc., Seabrook, NH 03874 USA) adjusted to pH 3 with approximately a 10 M HF solution (Fisher Scientific, Pittsburgh, PA 15219 USA). The adsorbed layer was then rinsed several times with a 2 mM HF solution (pH 3) or 0.1 mM KOH solution (pH 10) prior to evacuation and characterization in vacuum.

Voltammetric studies of each adsorbed alkenoic acid layer were performed in an electrolyte consisting of 10 mM KF adjusted to pH 3 with HF. All solutions were prepared from water pyrolytically distilled in pure O_2 through a Pt gauze catalyst (800 ° C). Prior to use of such solutions, blank experiments were performed in which the Pt(111) was immersed into the electrolyte followed by evacuation and Auger spectroscopy; the water evaporated without leaving a detectable residue or chemisorbed layer apart from the electrolyte species.

The alkenoic acids studied were of the general type $CH_2{=}CH(CH_2)_nCO_2H$, and were obtained as follows: 3-butenoic ("vinylacetic") acid (3BTA) and 6-heptenoic acid (6HPA) were obtained from Fluka Chemical Company, Inc. (Ronkonkoma, NY 11779 USA); propenoic ("acrylic") acid (PPA), 4-pentenoic acid (4PTA) and 10-undecenoic acid (10UDA) were obtained from Aldrich Chemical Co., Inc (Milwaukee, WI 53233 USA); each of these materials was used as received.

Electron energy-loss spectra (EELS) were obtained by means of an LK

Technologies EELS spectrometer (Bloomington, Indiana, 47405 USA). Beam current at the sample was approximately 120 pA; beam energy was 4 eV. The spectrometer was operated at a resolution of about 10 meV (80 cm^{-1}) in these experiments.

Packing densities, Γ_X (moles of adsorbed atoms/cm^2) or Γ (moles of adsorbed molecules/cm^2) were measured by two independent methods based upon Auger spectroscopy (beam current, 300 nA at 2000 eV, incident normal to the surface):

(i) Auger signals; I_X, due to each element X (X=C, O, K) were measured and normalized to the clean Pt(111) Auger signal at 161 eV. The elemental packing density was then obtained from $(I_X/I^0_{\text{Pt}_{161}})$ by means of eq. (1):

$$\Gamma_X = \left(I_X/I^0_{\text{Pt}_{161}}\right) \Big/ \left[B_X \sum_{i=1}^{N} L_i f_X^{M_i}\right] \tag{1}$$

where B_X is calibrated from adsorption studies of hydroquinone at Pt(111) [2x], $B_C = 0.314$ cm^2/nmol and $B_O = 0.574$ cm^2/nmol, and from KOH immersion study (29), $B_K = 3.03$ cm^2/nmol; L_i is the fraction of element X located at level i ($i = 1$ is adjacent to the surface and N is the outermost layer); f_X is the attenuation factor for Pt Auger electrons (235 eV) by a (3 × 3) layer of horizontally oriented hydroquinone [2a], and M_i is the number of non-hydrogen atoms located on the average path from the emitting atoms to the detector.

(ii) The Auger signal at 161 eV due to the Pt substrate was measured before (I^0_{Pt}) and after (I_{Pt}) formation of an adsorbed layer. Molecular packing density, Γ, is obtained from the ratio ($I_{\text{Pt}}/I^0_{\text{Pt}}$) by eq. (2):

$$\left(I_{\text{Pt}}/I^0_{\text{Pt}}\right) = (1 - J_1 K_X \Gamma) \times \ldots (1 - J_N K_X \Gamma) \tag{2}$$

where I_{Pt} and I^0_{Pt} are as described above, J_N is the number of non-hydrogen atoms in the Nth molecular layer and K_X is the equal to 0.165 cm^2/nmol for carbon and oxygen based upon the Pt(111)(3 × 3) adlattice of hydroquinone [2a].

Potassium alkeneoates used to take IR spectra were prepared by adding KOH (0.1 g) to an excess of the liquid alkeneoic acid (0.5 ml). After several hours, a white precipitate of potassium 4-penteneoate, potassium 6-hepteneoate, or potassium 10-undeceneoate was collected. Potassium 3-buteneoate was obtained by layering petroleum ether over a solution of KOH (0.2 g) in 3-buteneoic acid (0.5 ml) and collecting the crystalline product after several days. The salts were washed with petroleum ether. Potassium 6-hepteneoate was further purified by washing with acetone.

3. Discussion and results

In these experiments a Pt(111) surface, cleaned by Ar^+ ion-bombardment and annealed in ultra-high vacuum, was immersed into an aqueous solution containing an alkenoic acid adsorbate and a non-chemisorbing electrolyte (10 mM KF

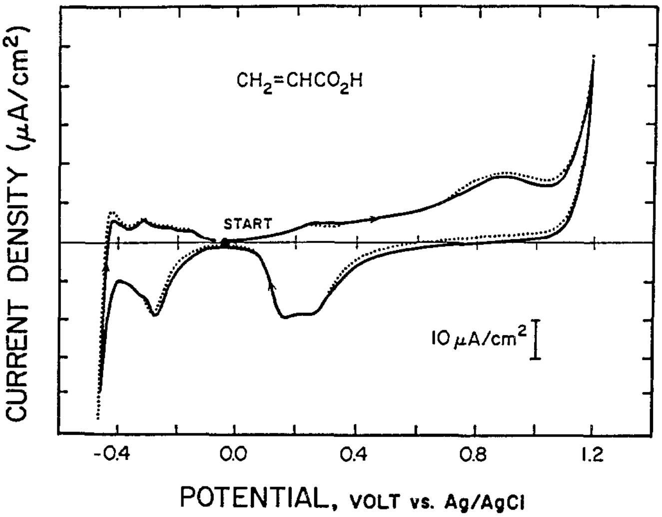

Fig. 1. Cyclic voltammetry of propenoic acid adsorbed at Pt(111). Solid curve: immersion into 1 mM or 0.1 mM aqueous solution of propenoic acid followed by rinsing with electrolyte. Dotted curves: as above, followed by 1 hour in vacuum prior to voltammetry. Experimental conditions: the clean, annealed Pt(111) surface was immersed into the electrolyte containing 1 mM propenoic acid; the electrolyte was 10 mM KF adjusted to pH 3 with HF; prior to voltammetry, the surface was rinsed with pure electrolyte; prior to evacuation the surface was rinsed with 2 mM HF (pH 3); during immersion and rinsing the surface was held at 0.1 V vs. the Ag/AgCl (1 M KCl) reference electrode; scan rate, 5.0 mV/s; temperature 23 ± 1° C.

adjusted to pH 3 with HF) at a controlled electrode potential (−0.1 V vs. Ag/AgCl reference). A chemisorbed layer was formed which was rinsed with pH 3 HF solution, and characterized by EELS, Auger spectroscopy, and cyclic voltammetry. Voltammetric experiments were performed using pure supporting electrolyte such that only a chemisorbed layer of the alkenoic acid was present. In order to verify that the adsorbed layer formed from solution is stable in vacuum, voltammetric experiments were performed in which the adsorbed layer was subjected to characterization (LEED, Auger, EELS) for a period of about one hour in vacuum prior to voltammetry. The fact that the two sets of voltammograms are identical, figure 1, is proof that irreversible changes in the nature and quantity of the adsorbed layer did not occur as a result of evacuation. The observed stability of adsorbed alkenoic acids is consistent with the general trend displayed by alkenes, alkynes, pyridines, mercaptans, thiophenes, aromatic hydrocarbons, phenols, and others: adsorbed species stable at Pt(111) in contact with solution are also stable in vacuum [2a–e,2g].

A principal thrust of the present work is electrochemical oxidation of adsorbed terminal alkenoic acids to form various unadsorbed products, as a function of the length of the aliphatic chain. Measurement of the number of electrons, n_{ox},

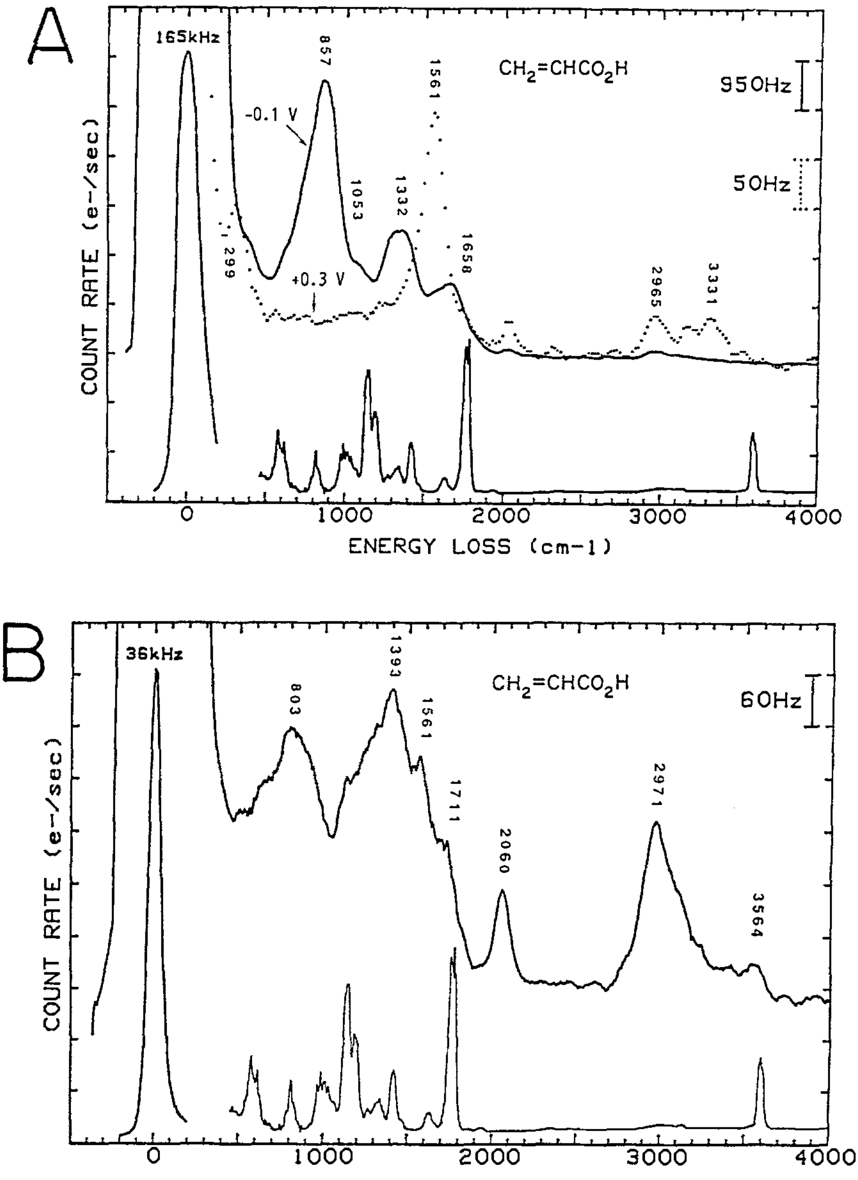

Fig. 2. Vibrational spectra of PPA adsorbed at Pt(111). A. (upper solid curve ———) EELS spectrum of PPA adsorbed at Pt(111), −0.1 V, pH 3; (upper dotted curve ······) EELS spectrum of PPA adsorbed at Pt(111), 0.30 V, pH 3. In A and B, the lower curve is mid-IR spectrum of PPA vapor at 200 ° C (6). B. (upper solid curve ———) EELS spectrum of PPA adsorbed at Pt(111) from the neat liquid, open circuit. C. (upper solid curve ———) EELS spectrum of PPA adsorbed at Pt(111), −0.1 V, pH 3 rinsed subsequently with KOH, pH 10. Lower curve is mid-IR spectrum of solid Na$^+$PPA$^-$ (7). Experimental conditions: EELS incidence and detection angle, 62° from surface normal; beam energy, 4 eV; beam current, ~120 pA; EELS resultion, 10 meV (80 cm^{-1}) fwhm.

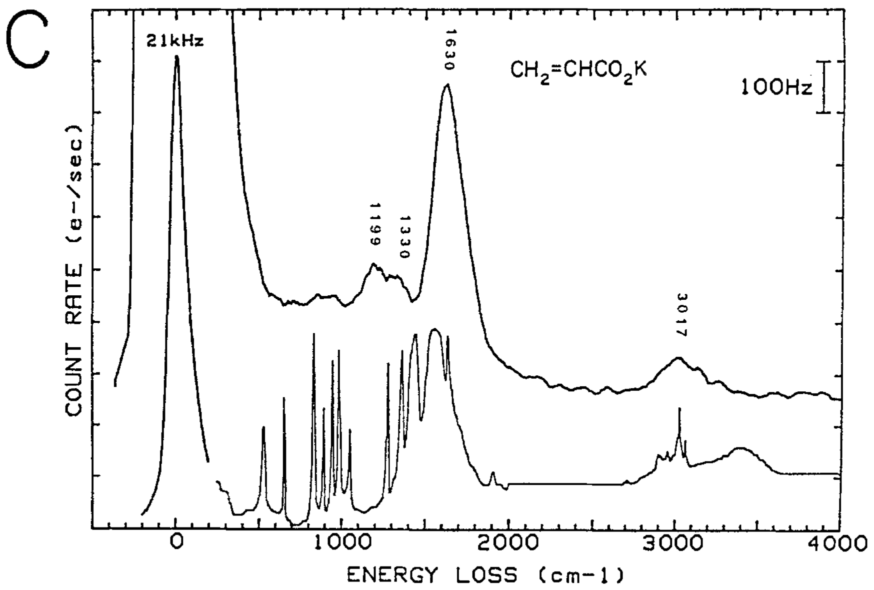

Fig. 2. (continued).

transferred during oxidation of each adsorbed molecule provides a first indication of the stoichiometry of the oxidation process:

$$n_{\mathrm{ox}}=\frac{Q-Q_{\mathrm{b}}}{FA\Gamma} \tag{3}$$

where Q is the faradaic charge to oxidize the Pt surface and adsorbed layer, Q_{b} is the charge to oxidize the clean Pt surface (approximation by the analogous charge in the second oxidative voltammetric scan), F is the Faraday constant, A is the geometric surface area of the Pt(111) electrode, and Γ is the molecular packing density of alkenoic acid (mol/cm^2). The results are presented in order of increasing chain length; that is, from three to eleven carbons per molecule.

3.1. PROPENOIC ACID (PPA)

Figure 1 (solid curve) shows the voltammogram for oxidation of adsorbed PPA, which occurs in a broad peak near +0.9 V. Also shown in the figure (dotted curve) is the result obtained when the adsorbed layer was characterized in vacuum for a period of one hour prior to voltammetry. As noted above, voltammetric results obtained with or without evacuation are virtually identical; the adsorbed PPA layer is stable in vacuum and does not undergo irreversible changes in the quantity or quality of its voltammetric behavior as a result of prolonged evacuation.

Table 1
Assignments (cm^{-1}) of EELS bands (cm^{-1}) for terminal alkenoic acids adsorbed at Pt(111)

Adsorption and rinsing at pH 3:

PPA		3BTA		4PTA		6HPA		10UDA		Description
−0.1 V	+0.35 V	−0.1 V	+0.3 V	−0.1 V	+0.2 V	−0.1 V	+0.2 V	−0.1 V	+0.2 V	
–	–	3571	3580	–	3551	–	–	–	–	O–H stretch
2979	2965	2960	3026	2980	2968	2963	2955	2961	2959	C–H stretch
2013	2031	–	2075	–	–	–	–	–	–	(CO)
1658	–	1734	1681	1730	1772	1719	1717	1720	1748	C=O, C=C stretch
–	–	1574	–	–	–	–	–	–	–	C=C stretch
–	1561	–	–	–	–	–	–	–	–	CO stretch (CO_2^-)
1332	–	–	–	–	–	–	–	1420	1430	C–H bend
–	–	1370	1485	1385	1390	1345	1371	–	–	C–H, O–H bend
1053	–	1174	1185	1179	1166	1216	1269	1103	1114	C–C, C–O stretch
857	–	895	895	879	914	878	877	907	964	vinyl C–H, OCO bend
–	–	661	689	725	682	654	654	650	665	OCO, C=C bend
–	–	556	558	–	541	–	–	–	–	CCO bend
–	–	–	–	504	–	–	–	–	–	CCO bend, Pt–C stretch
299	–	–	–	–	–	–	–	–	–	Pt–O stretch

Table 1 (continued).

Adsorption at pH 3; rinsing at pH 10 (−0.1 V)

PPA	3BTA	4PTA	6HPA	10UDA	Description
3017	2954	2967	2951	2946	C–H stretch
–	1739	1752	1710	1694	C=O, C=C stretch
1630	1574	1612	1607	–	C=C, CO_2^- stretch
–	1399	1389	1400	1386	C–H, O–H bend CO_2^- stretch
1330	–	–	–	–	CO_2^- stretch
–	–	1172	1168	1153	C–C, C–O stretch
955	914	928	1036	955	vinyl C–H bend
–	745	–	765	776	OCO bend
–	–	684	–	–	OCO, C=C bend
–	578	–	–	–	CCO bend
–	–	–	494	–	CCO bend, Pt–C stretch

Adsorption from neat liquid at open circuit:

PPA	3BTA	Description
3564	3575	O–H stretch
2971	2982	C–H stretch
2060	2036	(CO)
1711	1726	C=O, C=C stretch
1561	1605	C=C stretch
1393	1380	O–H, C–H bend
1150	1221	C–C, C–O stretch
803	924	vinyl C–H, OCO bend
655	680	OCO, C=C bend
–	550	CCO bend
514	–	CCO bend, Pt–C stretch

Experimental conditions: adsorption at Pt(111) from 10 mM aqueous KF solution (adjusted to pH 3 with HF) containing 1 mM, PPA, 3BTA, 4PTA (0.2 V) or 6HPA, or 2 mM 4PTA (−0.1 V), or saturated 10UDA, followed by rinsing with 2 mM HF (pH 3) or 0.1 mM KOH (pH 10) solution; other conditions as in figure 2.

The EELS spectra of PPA adsorbed on Pt(111) from aqueous fluoride solutions at negative and positive potentials, figure 2A and table 1, show striking differences: the overlapping C=C and C=O modes (1658 cm^{-1}) seen at −0.1 V gives way to a prominent carboxylate carbon-oxygen stretching peak (1561 cm^{-1}) at positive potentials. The carboxylate deformation band (857 cm^{-1}) also vanishes at positive potentials. The EELS spectra of adsorbed benzoic acid depend similarly upon potential [2g]. This is consistent with the expected horizontal orientations of adsorbed PPA and BA, which should induce coordination of the carboxylic acid moiety to the Pt surface. PPA adsorbed at negative electrode potentials displays EELS peaks corresponding to coordination through the C=C double-bond and *one* carboxylate oxygen, figure 2A, while adsorption at positive

Table 2
Auger and electrochemical data for alkenoic acids at Pt(111)

Compound	−log $C(m)$	Electrode potential, (Volt)	Ads. pH	Rinse pH	Normalized Auger Intensity			I_K/I^0_{Pt}	$(Q-Q_b)/(\mu C)/cm^{-2}$	
					I_C/I^0_{Pt}	I_O/I^0_{Pt}	I_{Pt}/I^0_{Pt}		Before vacuum	After vacuum
PPA	3.00	−0.1	3	3	0.415	0.393	0.675	–	678.5	615.4
PPA	3.00	0.3	3	3	0.455	0.313	0.640	–	–	693.1
PPA	3.00	−0.1	3	10	0.452	0.426	0.632	1.59	–	–
PPA	neat	open	–	–	0.482	0.299	0.678	–	–	–
3BTA	4.00	−0.1	3	3	0.529	0.370	0.617	–	918.5	884.2
3BTA	4.00	0.35	3	3	0.602	0.361	0.576	–	–	–
3BTA	3.00	−0.1	3	3	0.545	0.335	0.565	–	1090.8	898.5
3BTA	3.00	0.35	3	3	0.570	0.480	0.546	–	–	–
3BTA	3.00	−0.1	3	10	0.566	0.276	0.513	1.32	–	–
3BTA	neat	open	–	–	0.622	0.402	0.598	–	–	–
4PTA	4.00	−0.1	3	3	0.605	0.300	0.527	–	676.9	721.5
4PTA	4.00	0.2	3	3	0.571	0.580	0.564	–	–	–
4PTA	3.00	−0.1	3	3	0.601	0.330	0.570	–	–	–
4PTA	3.00	−0.1	3	10	0.720	0.293	0.524	0.639	–	–
6HPA	4.00	−0.1	3	3	0.820	0.177	0.437	–	786.2	847.6
6HPA	4.00	+0.2	3	3	0.750	0.290	0.500	–	–	–
6HPA	3.00	−0.1	3	10	0.888	0.134	0.474	0.647	–	–
10UDA	sat.	−0.1	3	3	1.076	0.110	0.355	–	846.2	915.4
10UDA	sat.	0.2	3	3	1.062	0.160	0.360	–	–	–
10UDA	sat.	−0.1	3	10	1.86	0.142	0.306	0.780	–	–

Experimental conditions: Pt(111) surface, Ar^+ bombarded and annealed (1000 K) in ultra-high vacuum; electrolyte, 10 mM KF adjusted to pH 3 with HF; surface was rinsed with 2 mM HF (pH 3) or 0.1 mM KOH (pH 10) prior to evacuation; incident electron beam, 300 nA at 2000 eV (cylindrical mirror analyzer); temperature 23 ± 1° C. The relative standard deviations for above measurements were between 3% and 7%.

Table 3
Packing densities of adsorbed alkenoic acids at Pt(111)

Compound	−log C(M)	Electrode potential (Volt)	Ads. pH	Rinse pH	Γ_C nmol/cm^2	Γ_O nmol/cm^2	Γ_K nmol/cm^2	Molecular F based on I_C/I_{Pt} nmol/cm^2	Molecular F based on I_{Pt}/I_{Pt} nmol/cm^2	n_{ox}	
										Before vacuum	After vacuum
PPA	3.00	−0.1	3	3	1.33	0.67	–	0.44	0.40	16.50	14.5
PPA	3.00	0.3	3	3	1.23	0.74	–	0.41	0.39	–	–
PPA	3.00	−0.1	3	10	1.44	0.74	0.53	0.48	0.45	–	–
PPA	neat	open	–	–	1.56	0.52	–	0.51	0.39	–	–
3BTA	4.00	−0.1	3	3	2.20	0.61	–	0.50	0.43	19.2	18.3
3BTA	4.00	0.35	3	3	2.26	0.63	—	0.54	0.49	–	–
3BTA	3.00	−0.1	3	3	2.05	0.59	–	0.52	0.50	22.0	18.1
3BTA	3.00	0.35	3	3	2.13	0.83	–	0.53	0.53	–	–
3BTA	3.00	−0.1	3	10	2.12	0.48	0.44	0.53	0.57	–	–
3BTA	neat	open	–	–	2.33	0.70	–	0.58	0.46	–	–
4PTA	4.00	−0.1	3	3	2.34	0.52	–	0.47	0.47	15.0	15.9
4PTA	4.00	0.2	3	3	2.21	0.58	–	0.44	0.42	–	–
4PTA	3.00	−0.1	3	3	2.33	0.57	–	0.47	0.42	–	–
4PTA	3.00	−0.1	3	10	2.80	0.51	0.21	0.51	0.54	–	–
6HPA	4.00	−0.1	3	3	3.62	0.30	–	0.52	0.49	15.7	16.9
6HPA	4.00	0.2	3	3	3.27	0.38	–	0.47	0.42	–	–
6HPA	3.00	−0.1	3	10	3.90	0.23	0.21	0.56	0.45	–	–
10UDA	sat.	−0.1	3	3	5.20	0.19	–	0.47	0.42	18.7	20.2
10UDA	sat.	0.2	3	3	5.13	0.29	–	0.47	0.42	–	–
10UDA	sat.	−0.1	3	10	5.35	0.16	0.26	0.49	0.53	–	–

Experimental conditions: Pt(111) surface, Ar^+ bombarded and annealed (1000 K) in ultra-high vacuum; electrolyte, 10 mM KF adjusted to pH 3 with HF; surface was rinsed with 2 mM HF (pH 3) or 0.1 mM KOH (pH 10) prior to evacuation; incident electron beam, 300 nA at 2000 eV (cylindrical mirror analyzer); temperature 23 ± 1° C.

potentials evidently leads to carboxylate coordination to the Pt surface through *both* oxygens (1561 cm^{-1}), figure 3A.

Auger spectroscopic data and formulas are given in tables 2–4. The saturation molecular packing density of PPA is 0.44 $nmol/cm^2$, which is close to that expected on the basis of molecular models [2g,4] of the horizontal orientation, 0.430 $nmol/cm^2$ (38.62 $Å^2$/molecule), figure 3A.

Use of eq. (3) and the coulometric charges obtained by integration of the voltammograms, figure 1 along with packing density data from Auger spectroscopy, led to n_{ox} equal to 14.5, compared with the expected value of 12 for complete oxidation to CO_2:

$$CH_2{=}CHCO_2H + 4H_2O \rightarrow 3CO_2 + 12H^+ + 12e^-. \qquad (4)$$

Adsorbed PPA retains K^+ ions strongly (0.53 $nmol/cm^2$ of K^+, and 0.48 $nmol/cm^2$ of PPA) when rinsed in a dilute KOH solution (pH 10). Evidently, PPA is adsorbed in anionic form and a counterion is present (H^+ or K^+, depending upon pH).

3.2. 3-BUTENOIC ACID (3BTA)

Voltammograms of adsorbed 3BTA at Pt(111) before and after one hour in vacuum are virtually identical, similar to fig. 1, indicating that the adsorbed material is stable.

A striking feature of the EELS spectrum of 3BTA adsorbed from acidic solution at a negative potential (−0.1 V), figure 4A, is the presence of a peak at 3571 cm^{-1} due to carboxylic acid O–H stretching. Evidently at negative potentials the carboxylic acid is pendant, but unable to hydrogen bond to its neighbors, figure 3B. A prominent carboxyl C=O stretch is also present at 1734 cm^{-1}, as expected.

3BTA is the only terminal alkenoic acid among those studied which displays a strong O–H stretching band. It is possible that this unique behavior is due to stabilization of the free carboxylic acid pendant by intramolecular hydrogen-pi bonding, as illustrated in fig. 3B, based upon spectroscopic evidence presented in ref. [9].

Adsorption of 3BTA at positive electrode potential (0.35 V) causes four-fold attenuation of the O–H stretching peak, figure 4B, and a significant decrease in packing density, tables 2 and 3. Evidently, a fraction of the carboxylic acid groups of the 3BTA layer interact with the Pt surface at positive potentials, leading to displacement of the acidic proton. Similar behavior is displayed by nicotinic acid, 3-thiophene carboxylic acid, and related compounds [2g,5], figure 3B. Fragmentation of a trace of the adsorbate to adsorbed CO (2050 cm^{-1}) is observed.

Treatment of the 3BTA layer with KOH at negative potentials leads to formation of the potassium salt, as evidenced by an Auger signal for potassium

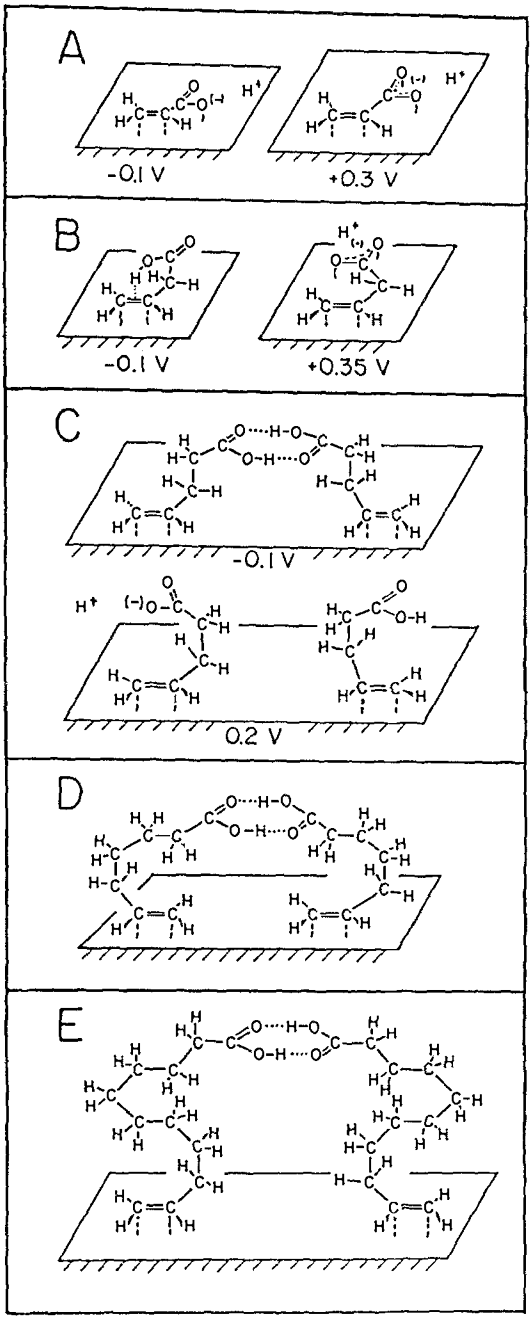

Fig. 3. Structural models of adsorbed alkenoic acids at Pt(111). A. PPA (adsorbed at −0.1 V, or 0.30 V). B. 3BTA (adsorbed at −0.1 V, or 0.35 V). C. 4PTA (adsorbed at −0.1 V, or 0.20 V). D. 6HPA (potential-dependence is negligible). E. 10UDA (potential-dependence is negligible).

Table 4
Formulas for obtaining packing density from Auger spectra

Compound	Formula
PPA	$\Gamma_C = (I_C/I^0_{Pt})/B_C$
	$\Gamma = \Gamma_C/3$
	$\Gamma_O = (I_O/I^0_{Pt})/B_O$
	$I_{Pt}/I^0_{Pt} = 1-5K\Gamma$
3BTA	$\Gamma_C = (I_C/I^0_{Pt})/B_C\left[\frac{1}{2}+\frac{f}{2}\right]$
	$\Gamma = \Gamma_C/4$
	$\Gamma_O = (I_O/I^0_{Pt})/B_O$
	$I_{Pt}/I^0_{Pt} = (1-3K\Gamma)^2$
4PTA	$\Gamma_C = (I_C/I^0_{Pt})/B_C\left[\frac{f^2}{5}+\frac{3}{5}f+\frac{1}{5}\right]$
	$\Gamma = \Gamma_C/5$
	$\Gamma_O = (I_O/I^0_{Pt})/B_O$
	$I_{Pt}/I^0_{Pt} = (1-3K\Gamma)(1-4K\Gamma)$
6HPA	$\Gamma_C = (I_C/I^0_{Pt})/B_C\left[\frac{2f^2}{7}+\frac{3f}{7}+\frac{2}{7}\right]$
	$\Gamma = \Gamma_C/7$
	$\Gamma_O = (I_O/I^0_{Pt})/B_O$
	$I_{Pt}/I^0_{Pt} = (1-3K\Gamma)^3$
10UDA	$\Gamma_C = (I_C/I^0_{Pt})/B_C\left[\frac{f^4}{11}+\frac{3f^3}{11}+\frac{2f^2}{11}+\frac{3f}{11}+\frac{2}{11}\right]$
	$\Gamma = \Gamma_C/11$
	$\Gamma_O = (I_O/I^0_{Pt})/B_O$
	$I_{Pt}/I^0_{Pt} = (1-3K\Gamma)^3(1-4K\Gamma)$
All Acids	$\Gamma_K = I_K/I^0_{Pt}/B_K$

Constants: $B_C = 0.314$ cm^2 nmol^{-1}; $B_O = 0.574$ cm^2 nmol^{-1}; $B_K = 3.03$ cm^2 nmol^{-1}; $K = 0.165$ cm^2·nmol^{-1}; $f = 0.70$.

(0.44 nmol/cm^2 of K$^+$, and 0.53 nmol/cm^2 of 3BTA), table 2, and an EELS spectrum characteristic of a carboxylate anion, figure 4C and table 1.

The packing density of 3BTA was 0.53 nmol/cm^2, compared with a theoretical value of 0.450 nmol/cm^2 based upon a model structure having a pendant carboxylic acid group as shown in fig. 3B. Packing densities and coulometric data, equation (3), indicate that $n_{ox} = 18.3$, corresponding to complete oxidation of adsorbed 3BTA to CO$_2$:

$$CH_2{=}CHCH_2CO_2H + 6H_2O \rightarrow 4CO_2 + 18H^+ + 18e\ . \tag{5}$$

3.3. 4-PENTENOIC ACID (4PTA)

A surprising characteristic of adsorbed 4PTA which is evident from the EELS spectrum, fig. 5A, is the virtual absence of a carboxylic acid O–H stretching band. On the other hand, the packing density of 4PTA, 0.47 nmol/cm^2, is as

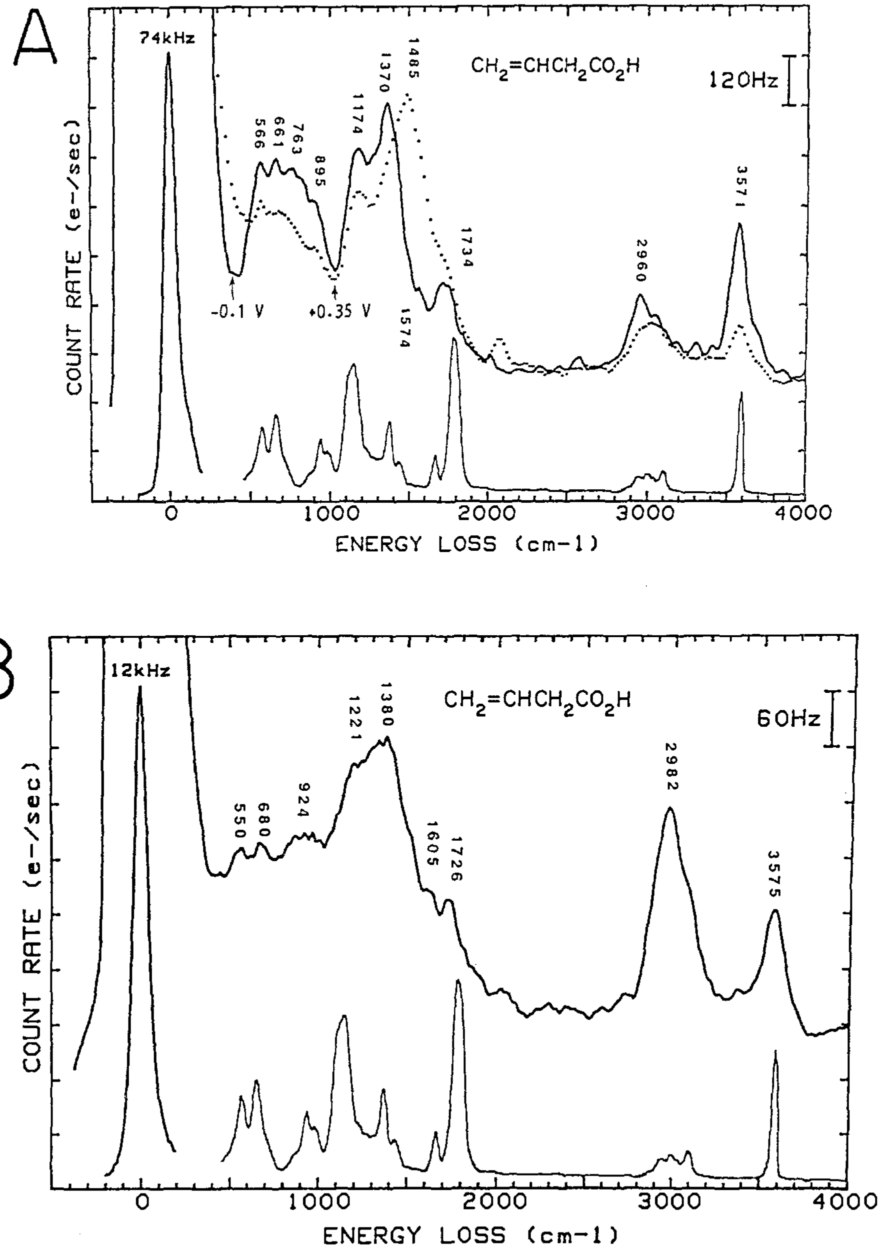

Fig. 4. EELS spectra of 3BTA adsorbed at Pt(111). A. (upper solid curve ——) EELS spectrum of 3BTA adsorbed at Pt(111), −0.1 V, pH 3. (upper dotted curve ······) EELS spectrum of 3BTA adsorbed at Pt(111), +0.35 V, pH 3. In A and B, the lower curve is the mid-IR spectrum of 3BTA vapor at 200 °C. (6). B. (upper solid curve ——) EELS spectrum of 3BTA adsorbed at Pt(111) from the neat liquid, open circuit. C. (upper solid curve ——) EELS spectrum of 3BTA adsorbed at Pt(111), −0.1 V, pH 3; rinsed subsequently with KOH, pH 10. Lower curve is mid-IR spectrum of solid K$^+$ 3BTA$^-$. Experimental conditions as in fig. 2.

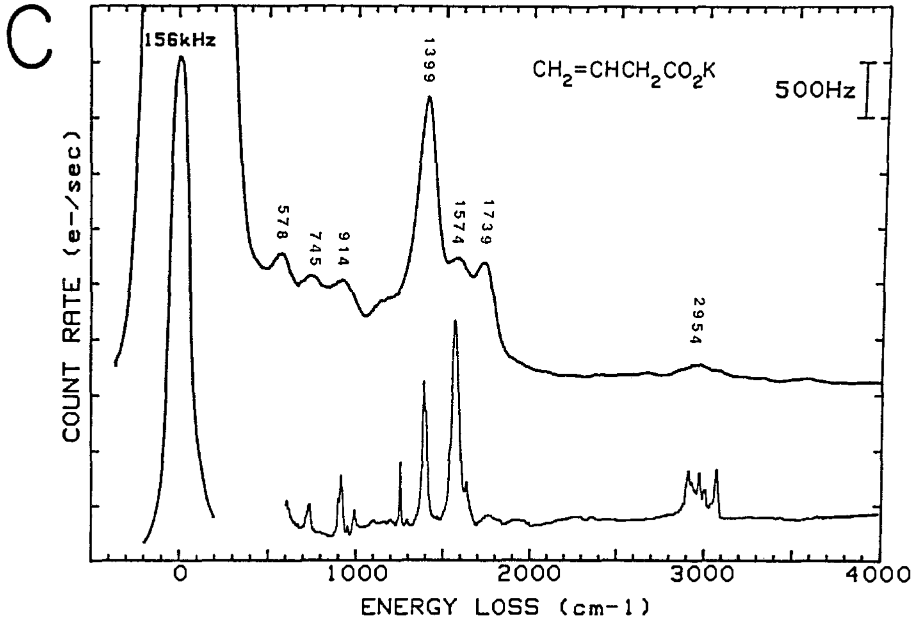

Fig. 4. (continued).

expected for a pendant carboxylate such as shown in fig. 3C. If the alkene and carboxylate moieties had both been bonded directly to the surface, the packing density would have been lower (about 0.2 nmol/cm^2). Evidently, the absence of an O–H stretching band is due to intermolecular hydrogen bonding between carboxylic acid groups, perhaps influenced by electrostatic interaction with the surface. Attachment to the surface is primarily through the C=C moiety; evacuation is not expected to dissociate the hydrogen bonds, and the spectra confirm this expectation. Because pendant carboxylate anions are present, rinsing the surface with KOH (pH 10) results in retention of K^+ ions (0.21 nmol/cm^2) although partial hydrolysis of the K^+ salt is evident from the presence of carboxylate C–O stretching (1612 cm^{-1}) bands, figure 5B. The EELS spectra of adsorbed 4PTA are influenced by the potential at which adsorption is carried out, figure 5A. At positive potentials the C–O stretching band (1179 cm^{-1}) is larger and CH bending (879 cm^{-1}) is smaller than at negative potentials. However, the carboxyl C=O stretching band (1772 cm^{-1}) is invariant to the potential of adsorption: evidently, the carboxylate moiety of 4PTA does not coordinate with the Pt surface. Intermolecular hydrogen bonding and ion-surface electrostatic interaction are evident from the EELS spectra, figure 5A. These findings indicate that intermolecular hydrogen-bonding and electrode-anion electrostatic interactions occur, as shown schematically in fig. 3C, although the structural details are not known.

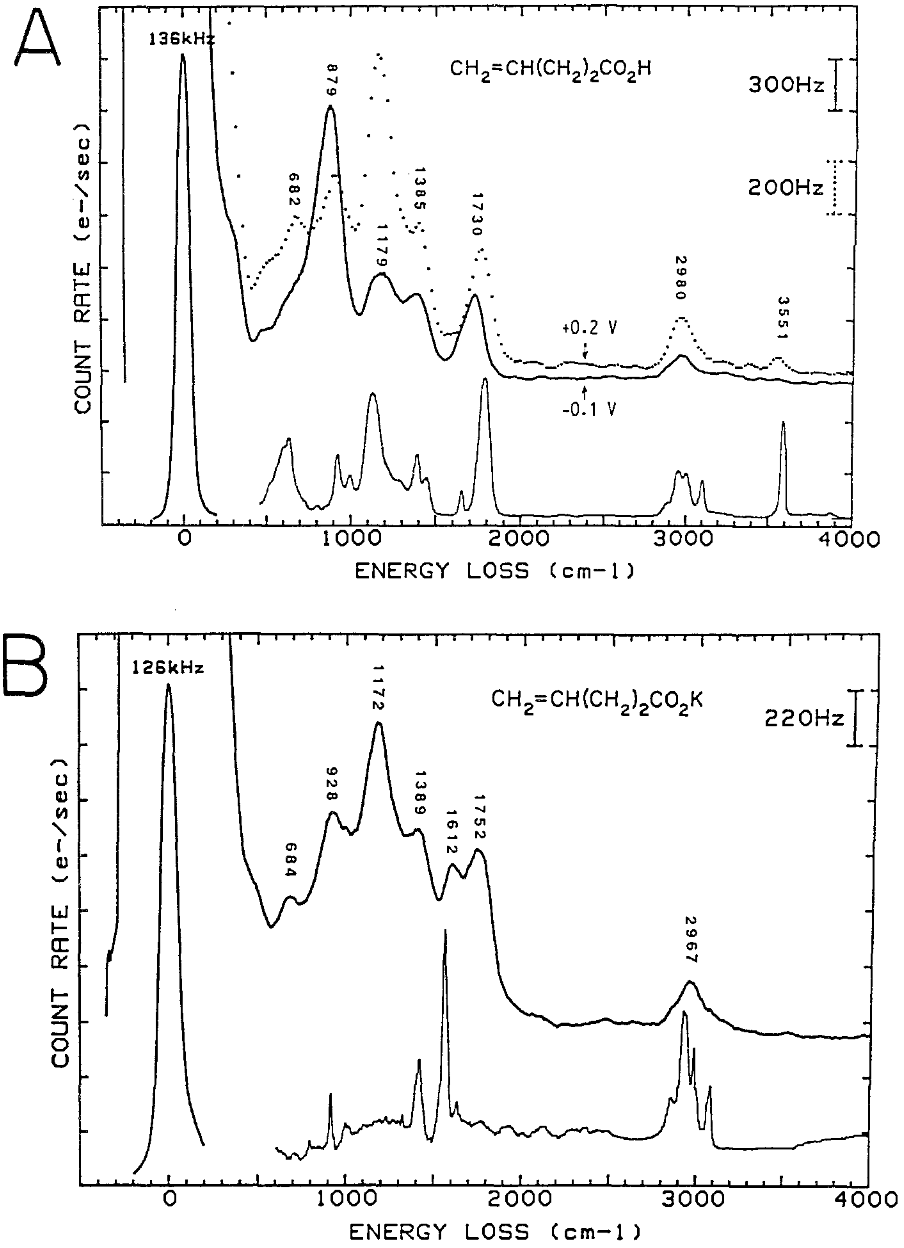

Fig. 5. EELS spectra of 4PTA adsorbed at Pt(111). A. (upper solid curve ———) EELS spectrum of 4PTA adsorbed at Pt(111), −0.1 V, pH 3. (upper dotted curve ······) EELS spectrum of 3BTA adsorbed at Pt(111), +0.2 V, pH 3. Lower curve is mid-IR spectrum of 4PTA vapor at 200 ° C (6). B. (upper solid curve ———) EELS spectrum of 4PTA adsorbed at Pt(111), −0.1 V, pH 3; rinsed subsequently with KOH, pH 10. Lower curve is mid-IR spectrum of K$^+$ 4PTA$^-$. Experimental conditions as in fig. 2.

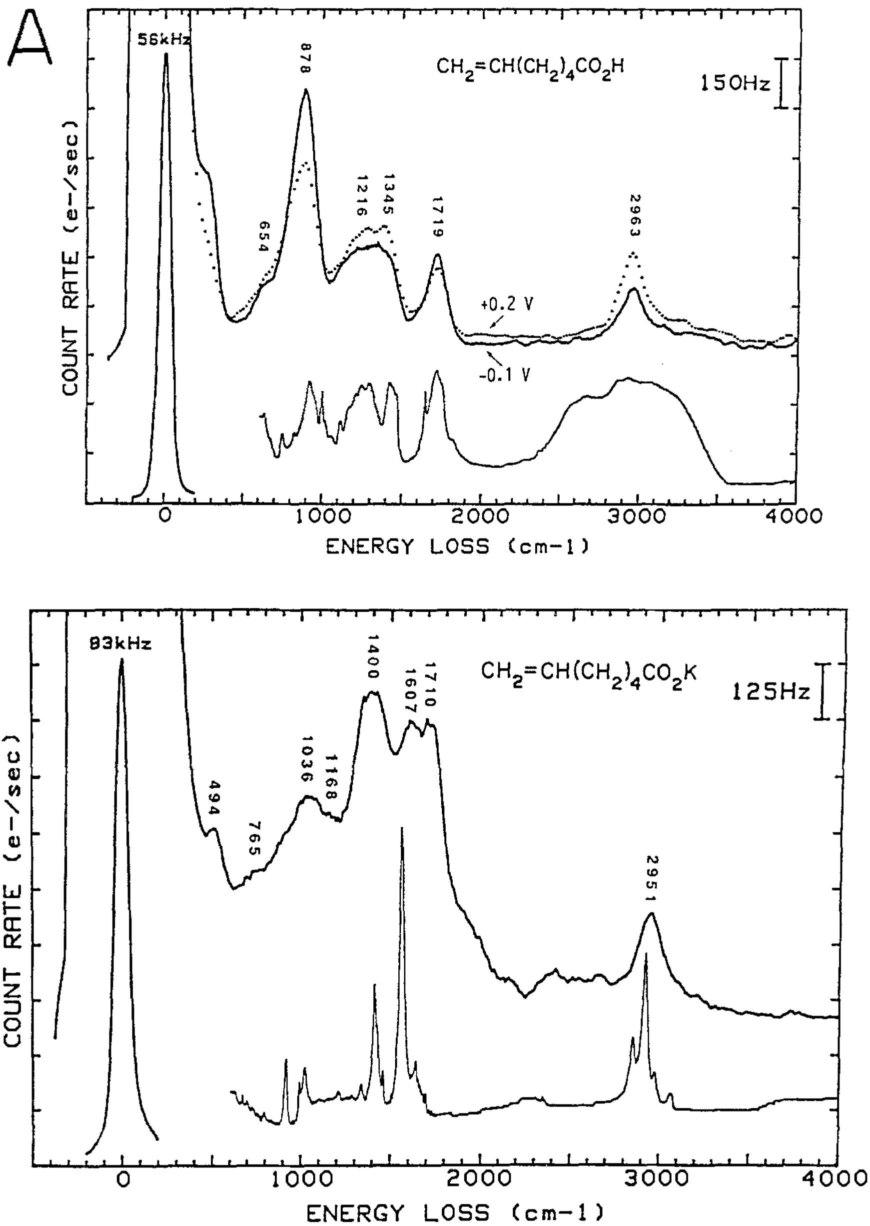

Fig. 6. EELS spectra of 6HPA adsorbed at Pt(111). A. (upper solid curve ——) EELS spectrum of 6HPA adsorbed at Pt(111), −0.1 V, pH 3. (upper dotted curve ······) EELS spectrum of 6HPA adsorbed at Pt(111), +0.2 V, pH 3. Lower curve is mid-IR spectrum of the neat 6HPA liquid (8). B. (upper solid curve ——) EELS spectrum of 6HPA adsorbed at Pt(111), −0.1 V, pH 3; rinsed subsequently with KOH, pH 10. Lower curve is mid-IR spectrum of K^+6HPA^-. Experimental conditions as in fig. 2.

Combining packing density data with coulometric charges for oxidation of adsorbed 4PTA, table 2 and eq. (3), leads to $n_{ox} = 15.9$, suggesting formation of CO_2 and malonic acid:

$$CH_2{=}CHCH_2CH_2CO_2H + 6H_2O \rightarrow 2CO_2 + HO_2CCH_2CO_2H + 16H^+ + 16e^-. \tag{6}$$

The observation that n_{ox} is smaller for 4PTA (15.9) than for 3BTA (18.3) is consistent with the fact that malonic acid is more stable towards electrochemical oxidation than oxalic acid, the probable oxidation intermediate of adsorbed 3BTA.

3.4. 6-HEPTENOIC ACID (6HPA)

EELS spectra of 6HPA at Pt(111) contain only a small carboxylic acid O–H stretching band (3380 cm^{-1}), figure 6A. As with 4PTA, the packing density of 6HPA, 0.52 $nmol/cm^2$, table 2, is indicative of horizontal orientation of the C=C moiety responsible for chemisorption, and vertical orientation of the pendant carboxylic acid group and aliphatic chain, figure 3D. Evidently, the absence of an O–H stretching band is a characteristic of adsorbed terminal alkenoic acids and is due to a combination of intermolecular hydrogen bonding and ion-electrode electrostatic interaction. The presence in the 6HPA layer of pendant carboxylate groups is indicated by retention of K^+ ions (0.21 $nmol/cm^2$ K^+, and 0.52 $nmol/cm^2$ 6HPA) when the adsorbed layer is rinsed with KOH (pH 10), tables 2 and 3.

Dependence of the EELS spectra of 6HPA upon the electrode potential during adsorption is slight, and is much less noticeable than for the shorter-chain homologs. Evidently, longer hydrocarbon chains lead to a larger electrode-anion distance and weaker interaction, as expected. The C–O stretching band (1216 cm^{-1}) is larger, and the C–H bending band (878 cm^{-1}) is smaller at the more positive potentials. This is the same trend as for the shorter acids but the changes are less noticeable. The vibrational frequencies are very similar at positive and negative potentials: C–H stretching (2963 cm^{-1}), C=O stretching (1718 cm^{-1}), overlapping C=C and C–O bands (1345 and 1216 cm^{-1}) and C–H bending (878 cm^{-1}), figure 6A. As with 4PTA, the carboxylate moiety of 6HPA is not coordinated to the Pt surface at any electrode potential, although ion-electrode electrostatic interaction is indicated by subtle changes in the EELS spectra.

The n_{ox} value for 6HPA is 16.9, as would be expected for oxidation to CO_2 and glutaric acid:

$$CH_2{=}CH(CH_2)_4CO_2H + 6H_2O \rightarrow 2CO_2 + HO_2C(CH_2)_3CO_2H + 16H^+ + 16e^-. \tag{7}$$

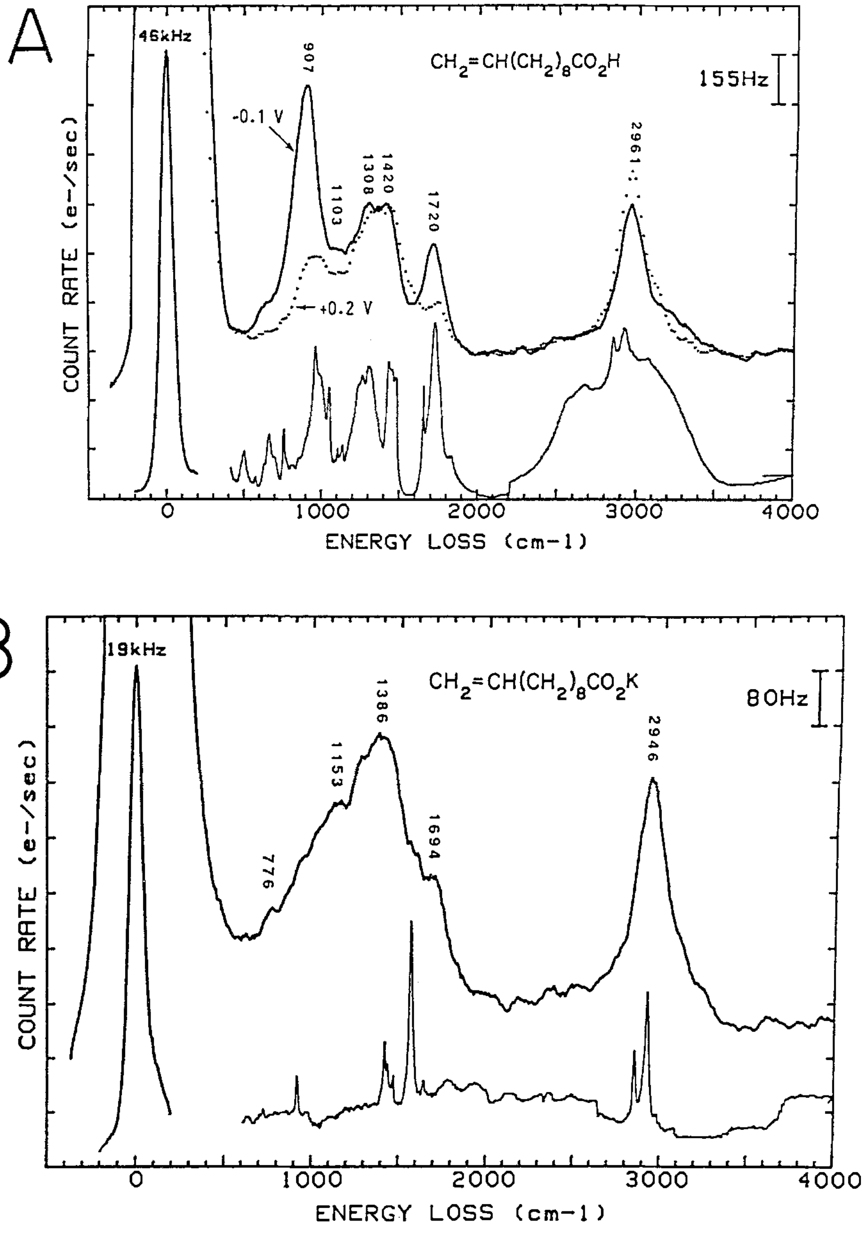

Fig. 7. EELS spectra of 10UDA adsorbed at Pt(111). A. (upper solid curve ———) EELS spectrum of 10UDA adsorbed at Pt(111), −0.1 V, pH 3. (upper dotted curve ······) EELS spectrum of 10UDA adsorbed at Pt(111), +0.2 V, pH 3. Lower curve is mid-IR spectrum of neat 10UDA liquid (8). B. (upper solid curve ———) EELS spectrum of 10UDA adsorbed at Pt(111), −0.1 V, pH 3; rinsed subsequently with KOH, pH 10. Lower curve is mid-IR spectrum of K^+ $10UDA^-$. Experimental conditions as in fig. 2.

3.5. 10-UNDECENOIC ACID (10UDA)

The behavior of 10UDA closely resembles that of 6HPA and continues the trends displayed by the other alkenoic acids. EELS data for 10UDA are given in fig. 7 and table 1. Voltammetric and Auger spectroscopic data are given in tables 2 and 3. The 10UDA layer retains K^+ ions less extensively (0.26 $nmol/cm^2$ K^+ and 0.49 $nmol/cm^2$ of 10UDA) than the shorter chain acids. As for 6HPA, the behavior of 10UDA suggests that intermolecular hydrogen-bonding within the adsorbed layer is extensive, but anion-electrode electrostatic interactions are relatively weak due to the long chain length and correspondingly large thickness of the intervening "hydrocarbon" layer, as illustrated schematically in fig. 3E. The n_{ox} value for 10UDA is 20.2, which is about as expected for oxidation of the adsorbed double-bond and one adjoining carbon:

$$CH_2{=}CH(CH_2)_8CO_2H + 6H_2O \rightarrow 2CO_2 + HO_2(CH_2)_7CO_2H + 16H^+ + 16e^-. \tag{8}$$

The difference between the observed n_{ox}, 20.2, and the expected value, 16, probably results from a slight error in calculation of the packing density of this long-chain adsorbate from Auger data.

4. Summary

Terminal alkenoic acids are strongly adsorbed at Pt(111) from aqueous inert (F^-) electrolytes, provided that the electrode potential is in the "window" between hydrogen adsorption and formation of Ptoxides/hydroxides. The adsorbed layer is stable in vacuum. The carboxylate moiety of 3BTA evidently interacts noticeably with the adsorbed C=C moiety by pi-hydrogen bonding [9]. Substantial interaction occurs between the carboxylate moiety of 3BTA and the Pt surface at positive but not at negative potentials. Intermolecular hydrogen-bonding predominates for the longer-chain acids. Surface attachment is predominantly through the C=C moiety. The C=C axis is parallel to the Pt(111) surface. Most or all of the C=C double-bond character of the acids is retained in the adsorbed state. The carboxylate moieties retain K^+ ions when exposed to 10^{-4} M KOH solution. Electrostatic interaction of the acids with the Pt surface decreases with increasing chain length and is barely noticeable for 6HPA and 10UDA. Electrochemical oxidation of adsorbed PPA and 3BTA proceeds completely to CO_2, while oxidation of 4PTA, 6HPA, and 10UDA produces $2CO_2$ and the appropriate diacid. Catalytic processes such as oxidation which proceed through a surface oxide or other adsorbed intermediate are thus expected to attack only the C=C moiety and perhaps are adjacent saturated carbon. However, reactions involving unadsorbed reagents are thus expected to selectively attack the pendant carboxylate groups. Intermolecular hydrogen-bonding is extremely strong in the five-carbon and longer adsorbed acids, while interaction of the carboxylate moiety with the surface predominates for the three-carbon and four-carbon acids.

The terminal alkenoic acids adsorb at Pt(111) to form an oriented layer in which C=C and one adjacent carbon are close to the surface while the fourth and higher carbons extend away from the surface. Accordingly, the packing densities (Auger data) and surface vibrational spectra (EELS) correlate closely with the IR spectra of the unadsorbed compounds and the pattern of electrochemical reactivity of the adsorbed species. These spectra, packing densities, and reactivities are very sensitive to electrode surface structure as shown in references 2d, 2f, 2i and 10.

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