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Hydrogenation of Oriented Monolayers of ω -Unsaturated Fatty Acids Supported on Platinum¹

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Abstract: Oriented monolayers of an ω -unsaturated fatty acid (17-octadecenoic acid, C18:1¹⁷) have been prepared at the air-water interface and transferred to the surface of clean platinum foils. When the platinum-supported monolayer is exposed to dihydrogen, the olefinic group of the acid is hydrogenated. The rate of this reduction can be varied over a range of 10^4 by changing the pH and metal ion concentration of the aqueous subphase on which the monolayer is prepared and the transfer pressure. The major influence on the rate is the metal ion incorporated into the monolayer: cadmium, an ion considered a catalyst poison, leads to slowly reduced monolayers; magnesium- and calcium-containing monolayers hydrogenate more rapidly; metal ion free monolayers reduce most rapidly. A secondary influence appears to be the rigidity of the film (as estimated by the compressibility of the original monolayer at the air-water interface). The rates of reduction of the supported unsaturated fatty acid monolayers parallel the rates of reduction of 1-pentene vapor on similar monolayer-covered foils. These observations collectively suggest a qualitative picture for fatty acid monolayers supported on platinum as thin, viscous, liquid or liquid-crystalline films. The study of the hydrogenation of supported, unsaturated monolayers provides an unexplored method for the examination of the microscopic structure of these films, and suggests new approaches to the study of mechanisms of heterogeneous hydrogenation.

Introduction

The research described in this paper has examined the hydrogenation of unsaturated fatty acids present as components of oriented monolayer films supported on platinum. This research has two related objectives: (1) to clarify the structure of oriented fatty acid monolayers on solid supports; (2) to explore the usefulness of these monolayers as probes with which to investigate mechanisms of heterogeneous hydrogenation. Oriented films of fatty acids and derivatives supported on solid substrates have been used previously in studies requiring thin organic films of known thickness or film component geometry; examples include geometrically defined systems for the study of energy transfer²⁻⁴ and photochemical reactions,⁵ catalysts for the heterogeneous photochemical cleavage of water,⁶ models for biological lipid membrane organization,^{7,8} and materials for X-ray diffraction gratings.⁹ Although the structures of oriented fatty acid monolayers at the air-water interface are reasonably well defined,¹⁰⁻¹² less is known about the structures of monolayers on solid supports. The physical characteristics which provide the basis for studies of monolayers at air-water interfaces—especially surface pressure-area isotherms and surface potentials—cannot be measured or are poorly defined for thin films supported on solids. Electron microscopy,⁷ infrared attenuated total internal reflectance spectroscopy,¹³ ellipsometry,¹⁴ and optical spectroscopy²⁻⁴ suggest that multilayer films are highly ordered, with the hydrocarbon chains in the all trans-zigzag conformation expected by analogy with the structures of crystalline fatty acids.¹³ The inferences drawn from these studies are convincing, but they are derived from observation of sample volumes containing multiple layers and large numbers of

molecules, and are pertinent only to the average structure of the multilayer assembly. Detailed information concerning the structure of supported monolayers is more difficult to obtain than that of multilayers for three reasons: first, the sensitivity of many of the spectroscopic techniques used with multilayers is too low to be used with a single monolayer; second, monolayers (and also the first layer of multilayer assemblies) seem to be intrinsically more heterogeneous than the outer layers of multilayers; third, the structure of a supported monolayer undoubtedly depends on the composition and morphology of the support surface. Even on smooth, uniform, glass supports, film balance studies,¹⁵ isotopic labeling,¹⁶ and electron microscopy¹⁷ suggest structural heterogeneity; on other supports (platinum,¹⁸ silver,¹⁹ mica^{19,20}) the structure of supported films is not well understood.

Despite present uncertainty concerning the structure of oriented, supported organic monolayers, these films appear to have great potential as mechanistic and structural tools with which to study many areas of surface chemistry. Organic monolayer films are materials in which both the molecular composition of the surface and the organization of the groups comprising the surface can, in principle, be controlled. The effective use of oriented monolayers as probes to study the mechanisms of heterogeneous catalysis or cellular adhesion requires that the information extracted about the structure and behavior of the monolayer components be sufficiently detailed at the molecular level to draw mechanistic conclusions. It is not evident that the physical and spectroscopic measurements traditionally applied in studies of oriented monolayers are capable of providing information of the type required for these potential new applications. This paper describes the initial stages of our effort to use the chemical reactions of monolayer

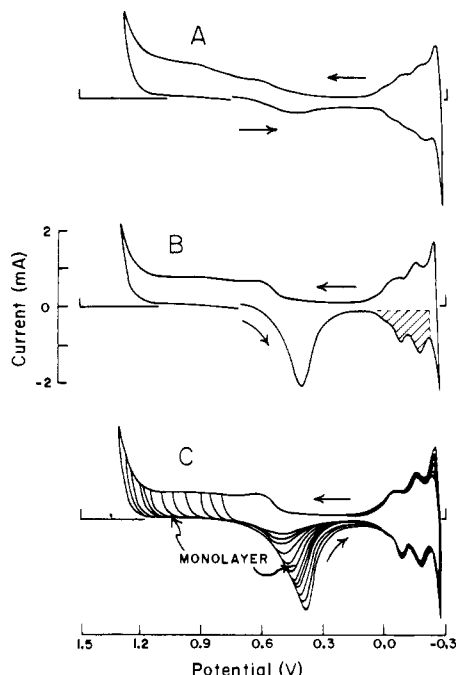
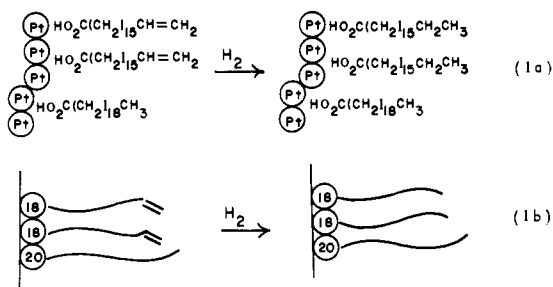


Figure 1. Cyclic voltammograms (room temperature, 1 M aqueous HClO_4 , 200 mV s^{-1}): A, the first scan obtained following immersion of foil cleaned at high temperature in the electrolyte; B, platinum foil after high-temperature treatment followed by ten electrochemical cycles between 1.3 and -0.2 V . This treatment was sufficient that subsequent scans were superimposed; C, reference scans of platinum as a function of the limiting anodic voltage. The voltammogram labeled "monolayer" in C is believed to correspond to the deposition and discharge of approximately one monolayer of surface oxides.

film components to explore simultaneously questions concerning film structure and surface reaction mechanisms.

The system we have examined is the hydrogenation of oriented, monolayer films of ω -unsaturated fatty acids and fatty acid salts on smooth platinum foils (eq 1a and 1b). Throughout



this paper we will use the convention in the lower equation to represent the transformation expressed in greater detail in the upper: a vertical line will represent the platinum surface; a horizontal line will represent the carbon backbone of the fatty acid; a circle will indicate the polar carboxylic acid or carboxylate salt head group. When necessary, the total carbon number of the acid will be indicated by a number in the circle representing the carboxyl group. In the text and tables, 17-octadecenoic acid, a C_{18} acid containing one double bond, will be abbreviated as $\text{C}_{18}:1^{17}$, *trans*-9-hexadecenoic acid, an internally unsaturated C_{16} acid, by $\text{C}_{16}:1^{9t}$, and eicosanoic acid, a saturated C_{20} acid, as $\text{C}_{20}:0$. Other acids will be named using analogous nomenclature. We have examined the rate of hydrogenation of the double bond on following exposure of monolayer assemblies of the type shown in eq 1 to dihydrogen as a function of several of the parameters—film pressure, subphase pH, and subphase metal ion concentration—which influence the structure of the monolayer. These experiments were intended to answer two specific questions.

(1) *Is the rate of monolayer hydrogenation determined by the structure of the film?* Rigid, nearly incompressible, structured films at the air-water interface are associated with high film pressures, high values of subphase pH, polyvalent cations in the subphase, and long fatty acid chains. If the rate of hydrogenation is influenced by the ease with which the double bond of the fatty acid can reach the platinum surface, and if the structure of a film supported on platinum is determined by that of the film at the air-water (A/W) interface from which it was prepared, it might be possible to correlate the rates of hydrogenation of the supported films on platinum with the structures of the films at the A/W interface. If the structure of the supported film is sufficiently disordered that its hydrocarbon portions resemble a liquid, independent of the structure of the film at the A/W interface, then other parameters (especially catalyst poisons) might have a greater influence on hydrogenation rates.

(2) *What can be inferred about the mechanism of heterogeneous hydrogenation from the reactivity of these films?* Hydrogenation of monolayer olefin films might give information about the reactivity of an initially clean, carbonaceous overlayer-free platinum surface.^{21,22} In these assemblies access of the olefinic units to the surface and lateral diffusion of these units across the surface are hindered, and this hindrance might be reflected in reactivity. Since the conditions of assembly of the supported monolayers can be controlled to introduce metal ions onto the platinum surface, rates of hydrogenation of supported monolayers might be useful in studying poisoning by metallic cations.

Results

Preparation and Characterization of Platinum Foil Supports.

The supports for the monolayer films were 0.051- or 0.10-mm thick, shiny platinum foils, cut into rectangles of ca. 20 cm^2 surface area. These dimensions dictated the use of polycrystalline platinum, but were necessitated by the requirement of a surface sufficiently large to support an easily analyzed quantity of fatty acid. A close-packed monolayer of oriented fatty acid contains ca. 5×10^{14} molecules/ cm^2 .¹¹ Thus, a single foil having a surface area of 20 cm^2 will support ca. 10^{16} molecules $\approx 16 \text{ nmol}$ of fatty acid. The kinetics that form the basis for this work require the ability to analyze reactions in which $<5\% = 0.8 \text{ nmol}$ of the starting fatty acid has been transformed. Losses in manipulating the sample during reaction and workup typically amount to ca. 30% of the sample. Thus, a representative analysis might require detection of 0.6 nmol of fatty acid. This quantity is within the capability of standard GLC techniques.

The surface of these foils was cleaned by one of two procedures: treatment with dioxygen at 900°C followed by reduction with dihydrogen at this temperature,²³ or electrochemical cycling between 1.3 and -0.2 V (vs. SCE).²⁴ The high-temperature procedure was used routinely; the electrochemical routine was used only to provide an occasional check that the surface cleaning procedure used had no significant influence on the monolayer hydrogenation kinetics. Following high-temperature reduction, the foils were cooled and ultimately transferred to the dipping trough used to prepare the oriented monolayer films. This transfer necessarily exposed the foils to the laboratory atmosphere. During this exposure the clean platinum surface adsorbed oxygen atoms. These oxides were readily apparent in a cathodic scan by voltammetry (see below). The foil surfaces were hydrophilic; although we have not explicitly measured contact angles for water on them, qualitative visual estimates suggest a value less than 20° .²⁵ Perhaps surprisingly, the foils showed no significant change in hydrophilicity and no evidence by cyclic voltammetry of surface contamination from oxidizable or reducible organic

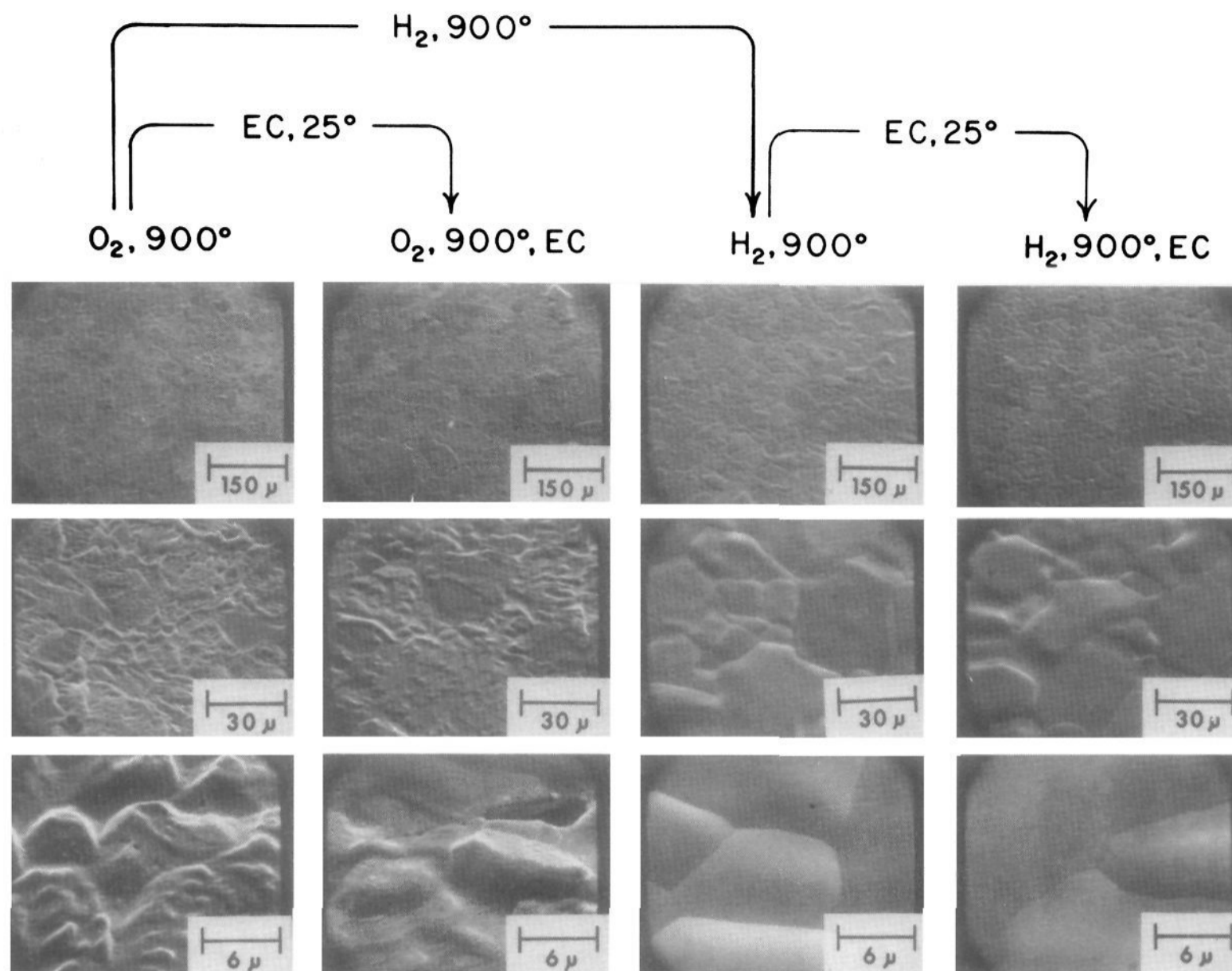


Figure 2. Scanning electron micrographs of platinum foils subjected to initial oxidation at high temperature (O_2 , 900°C , >24 h), followed by the further treatment indicated: [H_2 , 900°C] = reduction with dihydrogen at 900°C for >24 h; [EC, 25°C] = five electrochemical cycles at 200 mV s^{-1} between 1.3 and -0.2 V (vs. SCE, 1 M aqueous HClO_4 , 25°C).

compounds on exposure to the laboratory atmosphere for periods of several hours.^{23,26}

Two instrumental techniques have been used to characterize the foil surfaces: electrochemistry provided information concerning the presence or absence of adsorbed electroactive species on the foil surface, and an estimate of its surface area; electron microscopy gave an indication of the surface morphology. A typical cyclic voltammetric scan of a foil, cleaned by high-temperature oxidation and reduction followed by cooling, transfer into an electrochemical cell, and electrochemical cycling (ten times) between 1.3 and -0.2 V, is shown in Figure 1B. An indistinguishable cyclic voltammogram was obtained from foils that had been subjected only to electrochemical cycling without the high-temperature treatment. This voltammogram has the electrochemical features reported to be characteristic of a clean platinum electrode.²⁷ In particular, it shows no feature suggesting the occurrence of electrochemical processes other than the formation and discharge of surface oxides²⁷⁻²⁹ and hydrides.^{27,29} The voltammogram reproduced in Figure 1A was obtained from a foil cleaned at high temperature *without* intermediary electrochemical manipulation: this voltammogram was the first obtained after immersing the foil in the electrolyte. For reference, Figure 1C shows the development of surface oxides on a platinum foil (measured by the magnitude of the cathodic current between 0.8 and 0.6 V consumed in their reduction) as a function of the limiting anodic voltage used.³⁰ A monolayer of surface oxides is believed to correspond roughly to the indicated scan of Figure 1C.³¹ Comparison of this curve with Figure 1A suggests that the platinum surface obtained after transfer of a foil cleaned at high temperature through the laboratory atmosphere to the

electrochemical cell has considerably less than half a monolayer of surface oxides.

Integration of the current between 0.10 and -0.17 V in a cathodic scan (the shaded region in Figure 1B) allows the surface area of the foil to be estimated. Assuming that one hydrogen atom is adsorbed for each platinum surface atom, $210\ \mu\text{C cm}^{-2}$ corresponds to formation of monolayer coverage of adsorbed hydrogen.³² Overlap between peaks corresponding to hydrogen adsorption and dihydrogen discharge was corrected by dividing the integrated current shown in Figure 1B by the empirical factor of 0.80 recommended by Woods.³³ The surface roughness of the platinum foils derived using these data—that is, the ratio of the surface area estimated from hydrogen adsorption to the geometrical surface area—is 1.3 ± 0.2 . This value is in good agreement with previous estimates for smooth platinum electrodes,^{33,34} and is compatible with estimates for other materials.³⁵

Electron microscopy provides information concerning the surface morphology of the platinum foils. Figure 2 reproduces scanning electron micrographs of four platinum foils; each is shown at three magnifications. The starting material was foil that had been treated with dioxygen at 900°C for >24 h. The grain structure of the polycrystalline platinum is readily evident.³⁶ There are a small number of holes and cracks, concentrated along grain boundaries. Removal of the oxide film by electrochemical reduction at 25°C , followed by several cycles of electrochemical oxidation (at 1.3 V) and reduction (at -0.2 V), produces no significant change in the surface morphology. The surface roughness of the resulting oxidized film measured electrochemically by generation of adsorbed hydrogen is ~ 1.6 .

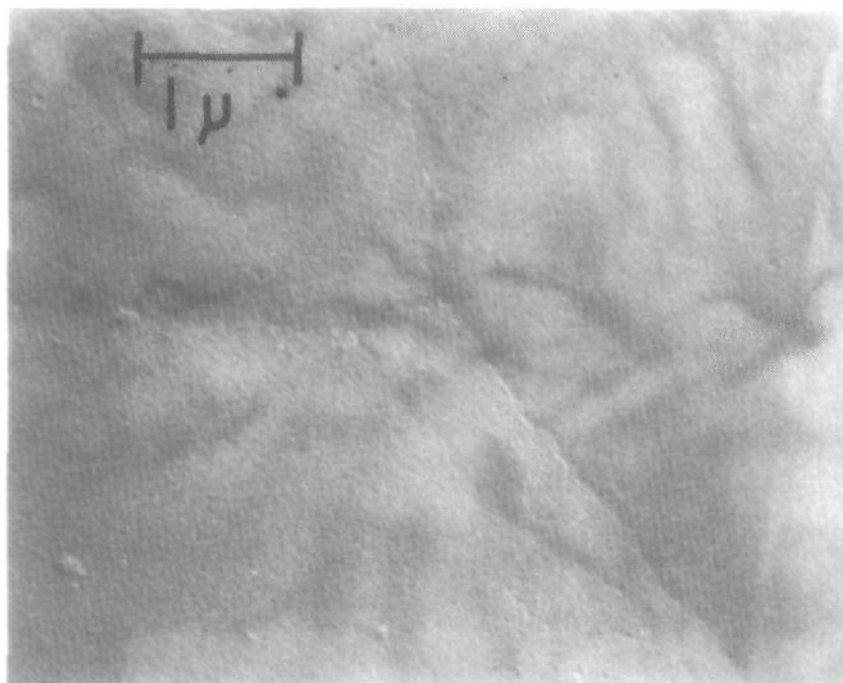


Figure 3. Transmission electron photomicrograph of a Parlodion replica of the region of intersection of three grains of a platinum foil cleaned by oxidation and reduction at high temperature.

Treatment of the oxidized film with dihydrogen at 900 °C for >24 h results in a marked smoothing of the surface. Electrochemical cycling at 25 °C results in no further change in the surface morphology. The only features visible at the highest magnification used are the grain boundaries.³⁷ Intragrain features having dimensions >40 nm would have been visible at this resolution. (The apparent finite width of the grain boundaries provides a practical measure of the instrumental resolution: in reality these boundaries are much narrower.) The surface of a foil reduced at high temperature was replicated and examined at higher resolution by transmission electron microscopy (Figure 3). This figure shows the intersection of three grains. The broad dark and light striations are probably artifacts of uneven shadowing. A large number of small features having a dimension of ca. 5 nm are, however, clearly evident, and the narrow grain boundary again provides a practical measure of the instrumental resolution (ca. 5 nm).

The combined electron microscopic and electrochemical data permit a number of conclusions concerning the surface of the foils used as supports for the monolayer films:

(1) The surfaces generated by the initial, high-temperature oxidation (used to remove oxidizable impurities) are macroscopically rough. This surface anneals on exposure to dihydrogen at high temperature, and becomes smooth on a macroscopic (>10 nm) scale: steps, kinks, voids, projections, and other surface features have dimensions <10 nm, with the exception of scattered, isolated irregularities and grain boundaries. We have no information on the predominant crystallite orientation at the surface after high-temperature annealing, or about the relative densities of ledges, kinks, and other surface features. Surface reconstruction of platinum at high temperatures is believed to expose predominantly the (100) face.^{38,39} The presence of peaks in the cyclic voltammograms at 0.02 and 0.12 V has, however, been suggested to be characteristic of exposed (100) and (111) faces, respectively.²⁹ Since these surfaces are used for catalytic hydrogenation—a reaction which is markedly insensitive to the surface structure⁴⁰—this uncertainty concerning the orientation of the exposed crystalline faces does not limit our interpretation of the kinetic data described below.

(2) The macroscopic morphology of the surface is not changed by limited electrochemical cycling. Surface areas estimated by electrochemical generation of adsorbed dihydrogen are thus probably not significantly influenced by the cyclic voltammetry used for their measurement. The observed

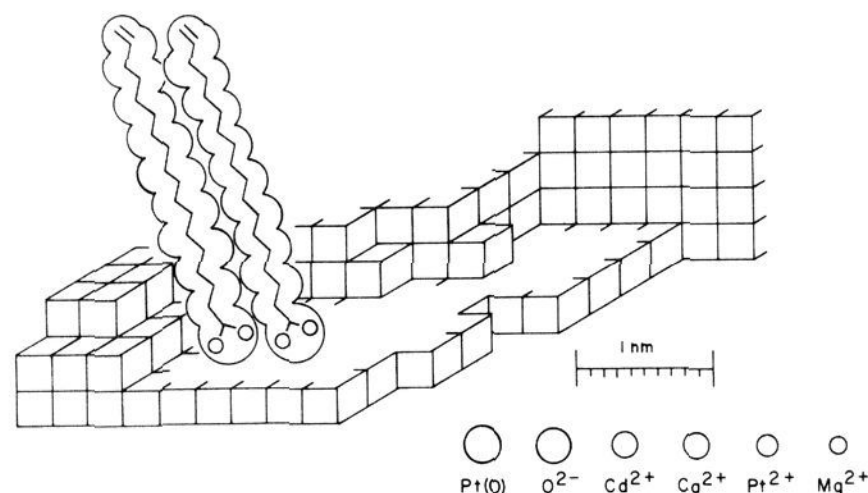


Figure 4. Schematic representation of a section of platinum surface compatible with surface roughness and electron microscopic data. For reference, sizes of several species used in this work are indicated.

roughness factor of 1.3 seems qualitatively compatible with the surface morphology visualized by electron microscopy.

(3) The surface is “clean”, in the sense that it has no macroscopically observable detritus, it shows no electroactive adsorbed species other than oxygen and hydrogen by cyclic voltammetry, and it is uniformly hydrophilic. It is certainly not clean in any sense recognized by surface high-vacuum physicists: it is, in fact, almost certainly completely covered by adsorbed oxygen, water, and (possibly) water-soluble, volatile impurities from the laboratory atmosphere. Since the foil is immersed in the aqueous subphase prior to monolayer transfer, however, atomic cleanness is neither required nor useful.

As an aid in visualizing the organization of supported monolayer films on platinum, Figure 4 suggests a schematic structure for a small region of a platinum surface which is compatible with the information available about the foils used in these experiments; typical structural features are represented approximately to scale. The area occupied by a single fatty acid molecule in a compressed monolayer at the air–water interface is approximately 0.19–0.20 nm² molecule⁻¹. The cross sectional area of a platinum(0) surface atom⁴¹ is 0.0770 nm², and that of a platinum(II) ion is 0.0256 nm².⁴² The carboxyl head group of a fatty acid thus covers a minimum of three platinum atoms. Many small features on the platinum surface—single atom vacancies, steps or kinks one or two atoms in size, single adatoms—will probably perturb the organization of the fatty acids to only a small extent, relative to that of a perfect crystal face of the same area. Surface structures of the size of the smallest features visible in the transmission micrograph (~5 nm) certainly will influence the organization of the fatty acid film. We do not know the distribution of irregularities on the platinum surface, but it seems probable that many of them are small and that a large portion of the surface accordingly appears to be almost as smooth to a fatty acid monolayer as would an extended terrace.

Efforts to visualize the fatty acid monolayers supported on platinum foils directly by scanning electron microscopy (SEM) were unsuccessful. Previous successful efforts to visualize mono- and multilayer structures have used transmission electron microscopy (TEM).^{7,43} TEM techniques are not applicable to our foils.

Assembly, Hydrogenation, Removal, and Chemical Analysis of Oriented Monolayer Films. Oriented films were prepared using procedures originally developed by Blodgett.^{2,3,11,44} The surface of the aqueous subphase in a circular dipping trough of the type developed by Fromherz⁴⁵ and Kuhn^{2,3} was cleaned by sweeping with the movable arms, and a clean platinum foil was immersed in the subphase. A mixture of the unsaturated fatty acid and a noninterfering saturated fatty acid (an internal GLC standard) was spread from a chloroform solution and compressed to the required surface pressure (usually 20 dyn

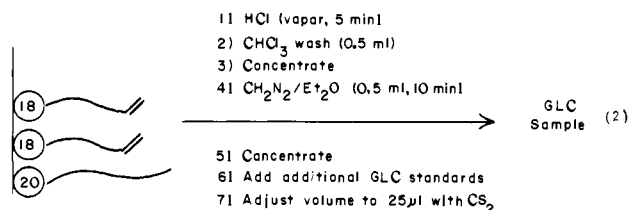
Table I. Control Experiments to Test the Reliability of the Procedures for Analysis of Fatty Acid Monolayers on Platinum

acids on foil, nmol ^a			H ₂ , min ^b	other conditions	acids detected, % ^c			$\frac{(C18/C20)_{final}^d}{(C18/C20)_{orig}}$
C20:0	C18:1 ¹⁷	C20:0			C20:0	C18:1 ¹⁷	C18:0	
3.49	0	13.1	0	<i>f</i>	85	<i>e</i>	80	0.94
1.74	6.84	9.07	0	<i>f</i>	66	56	69	0.97
2.92	2.72	12.0	0	<i>f</i>	89	73	94	0.88
3.06	11.8	2.83	0	<i>f</i>	48	28	44	0.62
3.39	13.6	0	1.0	<i>g</i>	63	60	2	0.98
3.46	13.9	0	0	<i>h</i>	61	54	0.3	0.89
5.66	21.8	5.23		<i>i</i>	96	98	96	1.0
8.17	7.62	33.6		<i>i</i>	95	93	96	0.98
3.14	13.7	0	~0.01	<i>j</i>	82	58	6.4	0.79

^a The quantities of acids present on the starting foil were estimated by measuring the area of monolayer transferred to the foil and the film pressure (and hence surface concentration of fatty acids (nmol/cm²)) and by assuming that the compositions of the films were the same as those of the fatty acid mixtures from which they were prepared. ^b Time of exposure of the assembly to dihydrogen, 1 atm pressure, 25 °C. ^c Yields are based on the quantities of acids present on the starting foils, and are estimated using internal GLC standards added just before GLC analysis. ^d This quantity is the ratio of total C18 species to C20 internal GLC standard originally applied to the foil, divided into the same ratio detected by GLC analysis after workup. ^e None detected. ^f Monolayer transferred to platinum at 20 dyn cm⁻¹; subphase pH 5.6, 1.5 mM CdCl₂. ^g Monolayer transferred to a clean glass microscope slide at 20 dyn cm⁻¹; subphase pH 5.6, 1.5 mM MgCl₂. ^h Monolayer transferred to platinum at 20 dyn cm⁻¹; subphase pH 1.8, 1.5 mM CdCl₂. ⁱ Analysis of a solution of fatty acids (CHCl₃). ^j Monolayer transferred to platinum at 20 dyn cm⁻¹, subphase pH 5.6, and exposed very briefly to dihydrogen.

cm⁻¹). The oriented film transferred to the platinum foil as it was pulled at 1 cm min⁻¹ through the A/W interface. The film pressure was maintained at a constant value (± 0.10 dyn cm⁻¹) during the transfer, and the area of the film transferred was monitored; as expected, this area was equal ($\pm 1-2\%$) to the geometrical area of the foil.^{18,19} The resulting assembly emerged dry from the dipping trough; its surface was hydrophobic. The assembly was suspended in a Fischer-Porter hydrogenation bottle, exposed to dihydrogen (1 atm, room temperature) for a chosen interval, removed, and worked up.

The workup and analysis used were, in principle, straightforward (eq 2). The monolayer was removed from the foil by



treating the assembly with HCl vapor and washing it with chloroform, the fatty acids were converted to methyl esters with diazomethane, additional GLC standards were added to facilitate determination of absolute yields, and the mixture was subjected to GLC analysis. A detailed description is given in the Experimental Section. Since, in practice, the quantities of materials involved were small, and since the cumulative error in the analysis was significant ($\pm 10\%$), several details concerning the procedure deserve explicit mention. First, if the procedure was carried through with a blank (i.e., if a saturated fatty acid was substituted for the unsaturated acid during the assembly of the monolayer), the relative quantities detected of this acid and the acid included in the monolayer as an internal GLC standard were reproducible to $\pm 6\%$ (Table I). The total recovery of these acids (measured relative to the second set of GLC standards added just before GLC analysis) was not reproducible: a representative recovery was 60%, but values ranged between 10 and 90%. Second, blank experiments carried through with known quantities of saturated and unsaturated fatty acids indicated that some fraction (10–30%) of the unsaturated acid was not removed in this workup procedure, perhaps because it adsorbed strongly on the platinum foil.^{46,47} Experiments in which known quantities of acids in solution were carried through the analysis scheme gave good yields and high accuracy.

The control experiments summarized in Table I lead to two summary conclusions concerning the removal and analysis of fatty acids from the platinum foils. First, analyses of the absolute yields of fatty acids are not sufficiently accurate to form the basis for kinetics, but analyses of the relative yields of fatty acids incorporated into a single supported monolayer are reasonably accurate. Second, analyses of the relative yields of unsaturated and saturated fatty acids are less accurate than analyses of relative yields of different saturated acids, presumably because of strong adsorption of the olefin to the surface. Studies of the kinetics of hydrogenation of unsaturated monolayer components were thus based on following the appearance of the corresponding saturated acid, relative to a saturated GLC standard included in the monolayer. Absolute yields of the monolayer components were also obtained routinely (using a separate GLC standard added just before injection onto the GLC), but were used only to monitor the recovery of acids. Representative experiments accounted for 40–70% of the fatty acids originally present on the platinum foils, with a typical value being 60%.

Rates of Hydrogenation of Unsaturated Fatty Acids in Monolayers on Platinum. The immediate objective of these kinetics studies was to examine the influence of the structural order of a monolayer supported on platinum on the rate of hydrogenation of its constituent unsaturated fatty acids. There is no established method of measuring the order within a supported monolayer; instead, in the preparation of the monolayers, we varied parameters (subphase pH, metal ion concentration, and surface pressure) known to influence the order (compressibility, phase) of the monolayers at the A/W interface, and assumed that conditions which generated rigid, highly ordered films on water would lead, after transfer to platinum, to supported films which were also relatively rigid. The correctness of this assumption is discussed below. Each point in a kinetics run represents a separate experiment, including all the steps from preparation of the platinum foil and transfer of the monolayer to GLC analysis of the hydrogenated fatty acid. As a consequence, these kinetics are sufficiently time consuming to discourage the testing of large numbers of possible combinations of parameters which might influence supported film structure.

Figure 5 summarizes the kinetics of hydrogenation of monolayers composed of a 4:1 mixture of C18:1¹⁷ (17-octadecenoic acid) and C20:0 (eicosanoic acid, GLC standard) as a function of the conditions at which the monolayer was transferred from water to platinum; each of these sets of experi-

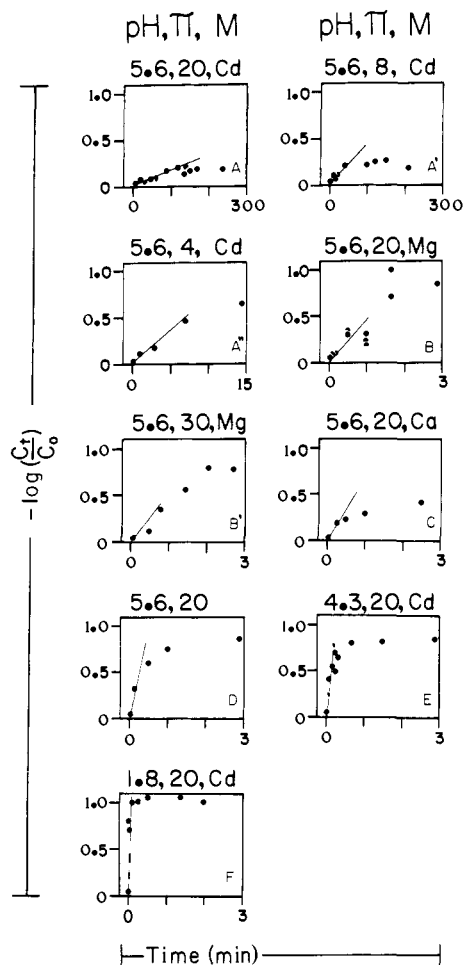


Figure 5. Kinetics of reduction by dihydrogen of C18:1¹⁷ (17-octadecenoic acid), supported as a mixed monolayer with C20:0 (eicosanoic acid) on platinum. The numbers above each plot refer to the conditions at which the monolayer was transferred from water to platinum: subphase pH, surface pressure, Π (dyn cm⁻¹), and subphase metal ion (1.5 mM, as M^{II}Cl₂). The line in each kinetic plot was used to approximate the initial rate of monolayer hydrogenation in estimating turnover numbers, N (ML).

ments is described in greater detail below. Rate data in Figure 5 are arbitrarily displayed as plots of $\log(C_T/C_0)$ vs. time, where C_0 is the initial concentration of C18:1¹⁷ and C_T the concentration at time T . These plots indicate that the reactions are not first order in olefin, even allowing for the significant experimental error in the measurements. The assumption of zero- or second-order kinetics gives no cleaner kinetics plots.

Figure 6 shows pressure–area isotherms for the mixture of C18:1¹⁷ and C20:0 on each of the subphases used in preparing the supported monolayers for hydrogenations. For calibration, this figure also gives the pressure–area isotherms for pure C18:0 and C18:1¹⁷ spread on an acidic subphase (pH 1.8). We have not proved that C18:1¹⁷ and C20:0 form ideal two-dimensional mixtures. The pressure–area isotherm of pure C18:1¹⁷ is almost identical with that of C18:0, and C18:0 and C20:0 form ideal mixtures.⁴⁸ Mixed monolayers of saturated and *internally* unsaturated fatty acids are, however, non-ideal.^{10,48}

A. pH 5.6, 20 dyn cm⁻¹, 1.5 mM CdCl₂. This film was the most rigid one we examined. For molecular areas greater than 0.2 nm², the pressure–area isotherm at the A/W interface was characteristic of a gaseous monolayer. For molecular areas less than 0.2 nm², the monolayer showed the low compressibility [$C = -A^{-1}(\partial A/\partial \Pi)_T$]⁴⁸ and steep increase in surface pres-

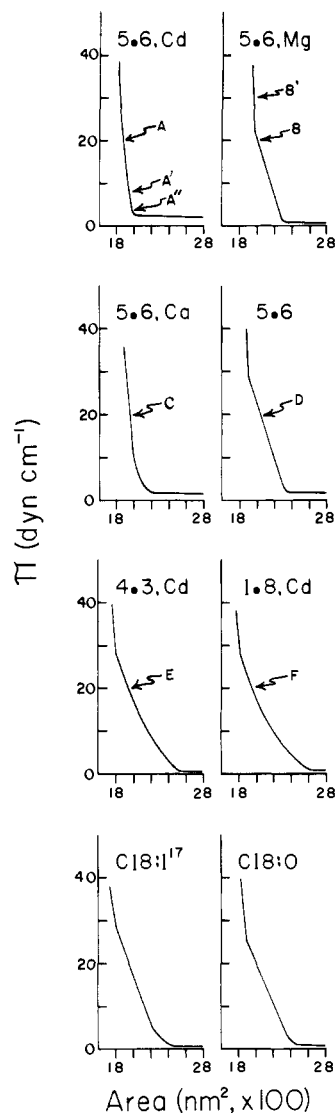


Figure 6. Surface pressure (Π)–area isotherms for 4:1 mixtures of C18:1¹⁷:(C20:0) on the indicated aqueous subphases and for pure C18:1¹⁷ and C18:0 on acidic subphases (pH 1.8). The surface pressures used during the transfers to platinum are indicated by the arrow on each curve. The letter labels refer to the kinetics curves in Figure 5.

sure with decreasing molecular area characteristic of a solid film. Above 25 dyn cm⁻¹ the monolayer collapsed slowly; the rate of collapse increased as the surface pressure increased. Monolayers were transferred at 20 dyn cm⁻¹ (0.188 nm²/molecule), well below the surface pressure at which rapid collapse occurs. Previous studies^{49,50} have indicated that condensed monolayer phases are indeed metastable and it is likely that the monolayer collapses at 20 dyn cm⁻¹. In practice, however, collapse occurred at a negligible rate relative to the time of the transfer process (approximately 5 min). The majority of the fatty acid present in the film was probably present as a Cd(II) soap, by analogy with other systems containing divalent ions.^{9,17,50,51} Increasing the subphase pH may lead to contraction of the monolayer in the presence of metal ions;⁵² the low average molecular area (0.188 nm²/molecule) observed at 20 dyn cm⁻¹ is, therefore, expected.

Hydrogenation of the monolayer supported on platinum converted 36% of the C18:1¹⁷ to C18:0 in ca. 2 h; no further hydrogenation occurred after this time. Cadmium is an effective poison for catalytic hydrogenation on platinum and other metal surfaces.^{53,54} The cessation of hydrogenation might have reflected a relatively slow surface poisoning reaction, or it might have indicated a structural heterogeneity in the sup-

ported monolayer film due to formation of cadmium soap complexes⁵⁵ or surface micelles.^{50,57} Evidence described below indicates that the foil is still active as a catalyst for the hydrogenation of 1-pentene present in the vapor phase after hydrogenation of the monolayer has stopped. Thus, the limited extent of hydrogenation observed for this monolayer probably reflects structural characteristics of the film, rather than a film-independent loss of catalytic activity.

A'. pH 5.6, 8 dyn cm⁻¹, 1.5 mM CdCl₂. This monolayer was transferred from the same aqueous subphase as that for A (above), but the transfer pressure was reduced to investigate the influence of an increase in monolayer compressibility on the hydrogenation rate. The general course of the hydrogenation was similar to that for A, but the initial rate of hydrogenation was approximately twice that for A.

A''. pH 5.6, 4 dyn cm⁻¹, 1.5 mM CdCl₂. This monolayer was transferred from the same aqueous subphase as A and A', but the transfer pressure was further reduced. This hydrogenation is appreciably more rapid than that of A or A' and proceeds to completion in ca. 30 min.

B. pH 5.6, 20 dyn cm⁻¹, 1.5 mM MgCl₂. The substitution of magnesium(II) for cadmium(II) in the aqueous subphase had two important effects on the hydrogenation of the monolayer after transfer to platinum: the rate of hydrogenation increased by approximately a factor of 10³ and the final conversion of C18:1¹⁷ to C18:0 increased to approximately 100%. The average molecular area (0.197 nm²/molecule) is only slightly larger than in A' (0.195 nm²/molecule); thus, it is likely that this parameter was not, by itself, responsible for the large difference in the behavior of the cadmium(II)- and magnesium(II)-containing monolayers.

B'. pH 5.6, 30 dyn cm⁻¹, 1.5 mM MgCl₂. The rate of hydrogenation of this monolayer is experimentally indistinguishable from that of B, although the transfer pressure corresponded to the solid region of the pressure-area isotherm.

C. pH 5.6, 20 dyn cm⁻¹, 1.5 mM CaCl₂. The pressure-area isotherm for this monolayer is similar to that for A, and the compressibility of the film at the A/W interface is indistinguishable from that of A at the transfer pressure. The initial rate of hydrogenation is, however, fast. The compressibility of the film cannot, therefore, be the sole determinant of hydrogenation rates.

D. pH 5.6, 20 dyn cm⁻¹, No Added Metal Ions. The pressure-area isotherm for this monolayer is similar to that for B, except that it has a slightly lower compressibility and a slightly larger molecular area (0.205 nm²/molecule vs. 0.192 nm²/molecule) at the transfer pressure. The initial rate of hydrogenation of the C18:1¹⁷ is approximately a factor of 1.5 faster than that for B; the extent of conversion is again essentially quantitative.

E. pH 4.3, 20 dyn cm⁻¹, 1.5 mM CdCl₂. At this pH, the extent of incorporation of cadmium into the monolayer should be small.^{7,50} The pressure-area isotherm suggests a fluid, compressible monolayer: the average molecular area (0.196 nm²/molecule) is significantly larger than that observed for the same cadmium chloride concentration and transfer pressure at pH 5.6 (A). The rate and extent of hydrogenation are again high.

F. pH 1.8, 20 dyn cm⁻¹, 1.5 mM CdCl₂. At this pH, the fatty acid should be present almost entirely in its protonated form, and very little or no cadmium should be incorporated.^{7,50} The rate of hydrogenation of C18:1¹⁷ in this fluid monolayer is the highest of the monolayers examined.

To test the sensitivity of these hydrogenation kinetics to changes in experimental conditions, a number of further control experiments were carried out. Hydrogenation of the usual mixture of C18:1¹⁷ and C20:0 (pH 5.6, 1.5 mM MgCl₂, 20 dyn cm⁻¹) on platinum foils that had been cleaned by high-temperature oxidation and reduction or by electrochemical

Table II. Turnover Numbers^a for Hydrogenation of C18:1¹⁷ on Platinum, $N(\text{ML})$, and for 1-Pentene on Platinum-Monolayer Assemblies, $N(\text{P})$

C18:1 ¹⁷		1-Pentene	
Sample	$N(\text{ML})$	Sample	$N(\text{P})$
A	0.001	a	200
A'	0.003	a'	230
A''	0.085	a''	1000
B	0.1	b	1300
B'	0.1	b'	1500
C	0.16	c	900
D	0.6	d	4000
E	1	e	3000
F	≥2	f	4000
			10 000 ^b

^a Turnover numbers have dimensions (molecules of olefin reduced)(platinum surface atom)⁻¹ min⁻¹. $N(\text{ML})$ was determined at $p(\text{H}_2) = 760$ Torr; $N(\text{P})$ was determined at $p(\text{H}_2) = 1300$ Torr. Control experiments for sample A indicated that $N(\text{ML})$ was independent of p_{H_2} from 100 to 1300 Torr. Comparable turnover numbers for hydrogenations on supported platinum are not available, but representative data are listed in ref 63 and 64. ^b Turnover number for 1-pentene on clean platinum with no surface monolayer of fatty acid.

cleaning between 1.3 and -0.2 V gave 80 and 72% reduction after exposure to dihydrogen for 1.7 min, respectively. The kinetics thus do not seem to depend on the specific details of the method used to clean the platinum foils. Variation in the pressure of dihydrogen between 25 and 1300 Torr gave no significant variation in yield (hydrogenation of the analogous fatty esters in ethyl acetate solution over reduced platinum also seemed to be independent of dihydrogen pressure at values between 750 and 1500 Torr). A foil treated with ethylene (57 Torr) and dihydrogen (1300 Torr) for 10 min *before* the monolayer containing C18:1¹⁷ and C20:0 was transferred to it (pH 5.6, 20 dyn cm⁻¹) showed the same extent of hydrogenation after 0.5 min as one that had not received the pretreatment: formation of a carbonaceous layer on the foil is apparently not a prerequisite to hydrogenation.⁵⁷ Transfer of a monolayer (18:1¹⁷ and 20:0, 4:1; pH 5.6, 1.5 mM MgCl₂, 20 dyn cm⁻¹) to a clean glass slide followed by exposure to dihydrogen resulted in no significant hydrogenation (Table I).⁵⁸

To facilitate comparisons among these hydrogenations and comparisons with other types of catalytic hydrogenations, we have estimated the equivalent of a catalytic turnover number $N(\text{ML})$ for each of these monolayers (Table II). The monolayer surface density for all of the films is ca. 5×10^{14} molecules cm⁻²; the corresponding surface density of platinum atoms is $1.1-1.3 \times 10^{15}$ cm⁻².^{42,59,60,61} For F, the monolayer is more than half reduced in the shortest interval in which we can expose the foil to hydrogen (ca. 1 s). Thus, the minimum "turnover number" for this system is $N(\text{ML})_{\text{F}} \approx 2$ molecules min⁻¹ (platinum atom)⁻¹. The actual number may be higher, since neither the time required for dihydrogen to reach the platinum surface nor the rate of reduction of platinum surface oxides to platinum is known.⁶² Corresponding numbers for the other films are listed in Table II. Each of these numbers is based on estimates of initial rates from the data of Figure 5; these estimates are indicated on the plots of this figure by straight lines. Since the scatter in the data is large, and since the kinetics follow no simple rate law, the turnover numbers provide only qualitative estimates of relative rates. It may be a misnomer to call these estimates "turnover numbers", since there are more platinum centers than substrate olefins, and it is not evident that any platinum atom acts catalytically. Nonetheless, these numbers can be compared with turnover

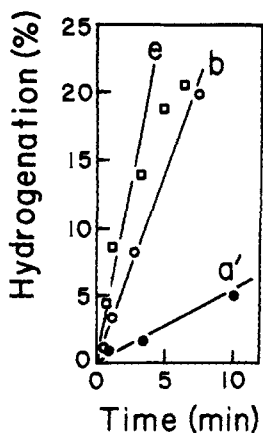


Figure 7. Representative kinetics plots for hydrogenation of 1-pentene on platinum foils covered with oriented monolayers of a 4:1 mixture of C18:1¹⁷ and C20:0 (the subphase composition and transfer pressure used in preparing the foils is the same as that used in corresponding studies of monolayer hydrogenation).

numbers for conventional catalytic hydrogenations, which range from 1 to >1000 molecules min^{-1} (platinum atom)⁻¹ for mono- and disubstituted olefins on platinum at corresponding temperatures and dihydrogen pressures.^{63,64}

At the simplest level of discussion, these kinetics experiments establish that it is possible to determine the rate of hydrogenation of an olefinic fatty acid component in a supported monolayer film on platinum, and suggest that the magnitude of this rate is influenced by catalyst poisons incorporated into the monolayer. Several other, more qualitative, experiments also contribute to an understanding of monolayer structure and its influence on the reactivity of its components.

Catalytic Hydrogenation of Olefins Present in the Vapor Phase Using a Platinum Foil-Fatty Acid Monolayer Assembly. The rate of reduction of the olefinic components of the supported monolayers is lower than the rate of reduction of small, unconstrained olefins on platinum. This difference might originate in the influence of the carboxylic acid head groups and associated metal ions in modifying the activity of the platinum surface (acetate ion is a moderately active catalyst poison on platinum⁶⁵), or it might reflect a constraint imposed on the olefinic groups by the structure of the oriented monolayer which would hinder their approach to the catalyst surface. In an effort to suggest which of these hypotheses was the more plausible, we examined the reduction of an olefin, or a mixture of two olefins, originally present in the vapor phase, using as catalysts platinum foils bearing monolayers.

Representative plots of the initial rate of conversion of 1-pentene to *n*-pentane ($p(\text{H}_2) = 1300$ Torr, $p(1\text{-pentene}) = 80$ Torr) at platinum foil surfaces are shown in Figure 7. Turnover numbers were estimated from these initial rate plots, and are summarized in Table II. The most active catalyst was a clean platinum foil: the turnover number for hydrogenation of 1-pentene is $N(P) \sim 10\,000$ molecules min^{-1} (platinum atom)⁻¹. The least active ($N(P)_{\text{Cd}} \sim 170$) was a foil that had been dipped into 1.5 mM CdCl₂ solution (pH 5.6), withdrawn, and dried. Platinum foils modified by oriented monolayers of the 4:1 mixture of C18:1¹⁷ and C20:0 prepared under conditions analogous to those used previously in the study of monolayer hydrogenation have intermediate activity. We denote monolayers prepared using the same aqueous subphase and transfer pressure as was used previously for a monolayer of C18:1¹⁷ by the corresponding lower-case letter. The reactions are initially zero order in olefin.

Two features of these data are pertinent to the origin of the differences in rates of hydrogenation of the unsaturated components of the various monolayer films. First, the foil

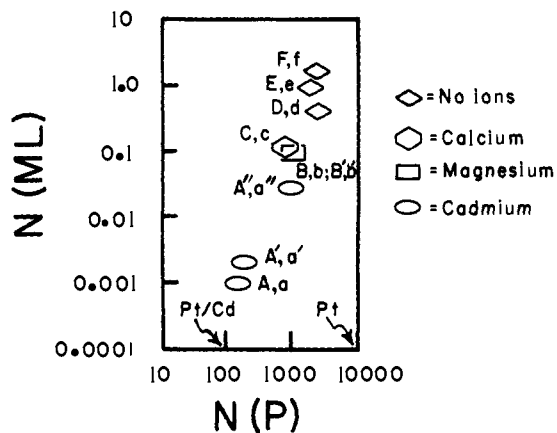
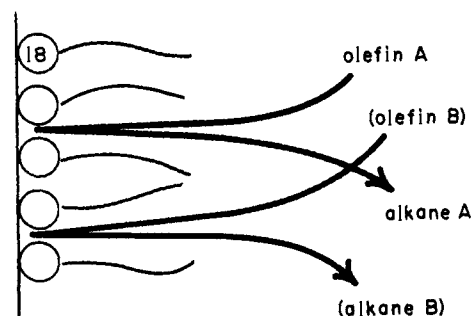


Figure 8. Correlation between $N(\text{ML})$ (the turnover number for hydrogenation of monolayer components) and $N(P)$ (the turnover number for hydrogenation of 1-pentene on monolayer-covered foils). The rates of hydrogenation of 1-pentene on clean platinum (Pt) and on platinum that had been dipped in aqueous 1.5 mM CdCl₂ solution (Pt/Cd), withdrawn, and dried are indicated by arrows along the $N(P)$ axis.

covered with monolayer *a* is still catalytically active in the hydrogenation of 1-pentene after the C18:1¹⁷ present in monolayer A has ceased to hydrogenate. The interpretation of the kinetics of hydrogenation of 1-pentene on the monolayer-covered foil is complicated by incomplete understanding of the uniformity with which the film is distributed over the foil. If there are holes in the monolayer, some fraction of the hydrogenation of 1-pentene may be occurring on bare platinum metal. Nonetheless, the observation that a foil covered with monolayer *a* is catalytically active in hydrogenation of 1-pentene *after* it has become inactive in hydrogenation of the monolayer establishes that at least some of the surface has not been poisoned by cadmium, and indicates that the *lateral* diffusion of the unsaturated acids of monolayer A is too slow to permit their access to catalytically active regions. Second, the turnover numbers for hydrogenation of monolayer components, $N(\text{ML})$, correlate with those for hydrogenation of 1-pentene on foils covered with the monolayer, $N(P)$ (Figure 8); the values of $N(P)$ are, however, larger than those for $N(\text{ML})$ by 10^3 – 10^5 , and are less sensitive (by approximately a factor of 10^2) to changes in the composition of the monolayer. Thus, hydrogenation of olefins in the monolayer and in the vapor are similar reactions, and their rates are influenced in parallel by changes in monolayer composition.

These experiments indicate that the presence of a monolayer on a platinum surface influences the rate of hydrogenation of an external olefin. We briefly explored the possibility that it might be possible to modify the *selectivity* of platinum toward olefins using monolayer films. Competitive hydrogenation of mixtures of two olefins in the vapor phase using as catalyst either a clean platinum foil or a foil bearing a monolayer similar to *b* (C18:0, subphase pH 5.6, 1.5 mM MgCl₂, $\Pi = 20$ dyn cm^{-1}) showed no difference in selectivity (eq 3, Table III).

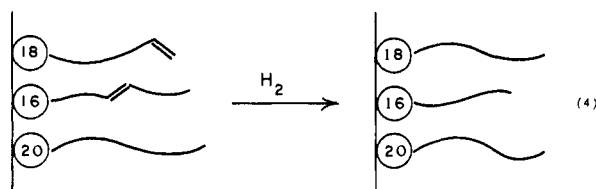


(3)

Table III. Competitive Hydrogenations of Pairs of Olefins on Clean and Monolayer-Covered Platinum Foils

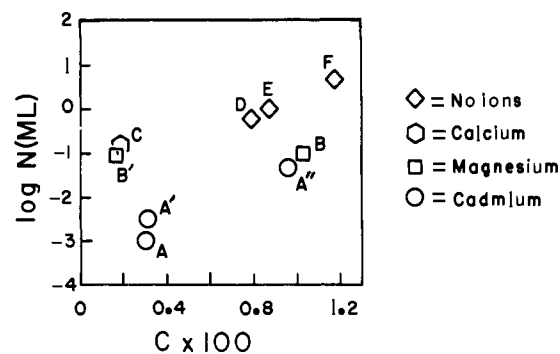
olefin		k^A/k^B	
A	B	clean	monolayer
1-hexene	tetramethylethylene	>100	>100
1-hexene	cyclohexene	~5	~4
1-pentene	cyclopentene	~1.4	~1.4

Hydrogenation of Mixtures of 17-Octadecenoic Acid and *trans*-9-Hexadecenoic Acid. A mixture of these two acids (C18:1¹⁷ and C16:1⁹) and C20:0 as a GLC standard (7:7:4 mole fraction) was spread from chloroform on an aqueous subphase (pH 5.6, 1.5 mM MgCl₂), transferred to platinum at a surface pressure of 20 dyn cm⁻¹, and hydrogenated (eq 4). This mixture of fatty acids did not form a stable monolayer

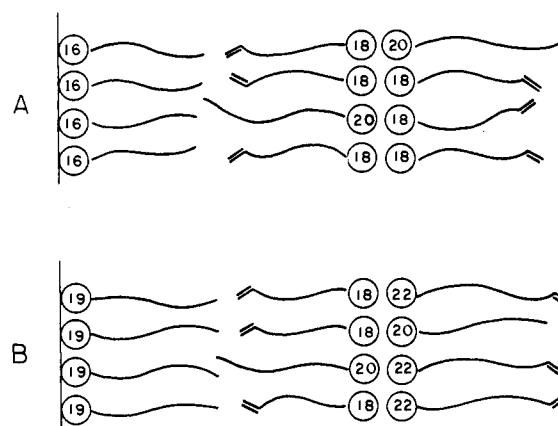


at the air-water interface. Collapse occurred at a significant rate at any pressure above the equilibrium spreading pressure (~ 1 – 2 dyn cm⁻¹),⁶⁶ and at 20 dyn cm⁻¹, the surface area of the compressed film decreased approximately 5% min⁻¹. The transferred film, in this instance, probably consisted of mixtures of mono- and multilayer regions. Interpretation of the experiment is further complicated by the fact that the two unsaturated acids form a nonideal mixture.⁴⁸ Nonetheless, several observations concerning this system are relevant. First, the film was qualitatively very fluid at the air-water interface, and the rate of hydrogenation of its olefinic components after transfer to platinum seemed qualitatively to be high. Second, if the hydrogenation was interrupted (20 s after admission of dihydrogen to the hydrogenation apparatus), the yields of C18:0 and C16:0 were 53 and 75%. Thus, the internal olefin hydrogenated slightly more rapidly than the terminal olefin. In homogeneous solution in ethyl acetate, the terminal olefin hydrogenated ca. ten times more rapidly than the internal olefin, in agreement with results from simpler systems.⁶⁷ Several possible interpretations are possible for these results. For example, the double bond of C16:1⁹ is closer to the platinum surface than that of C18:1¹⁷, and may thus react more rapidly at the surface. Alternatively, phase separation may have occurred in this two-olefin system, and the rigidity of the film may vary from one phase to the other. Since monolayers of internally unsaturated olefins are usually more expanded than their saturated analogues (and, by analogy, than 17-octadecenoic acid), the more condensed (and more slowly hydrogenated) phase would be expected to be enriched in the terminally unsaturated olefin, and the less condensed (and more rapidly hydrogenated) phase would be enriched in the internally unsaturated olefin.

Hydrogenation of Components of Multilayer Films. Two trilayers containing unsaturated components were assembled. The first (transferred from an aqueous subphase, pH 5.6, 20 dyn cm⁻¹, 1.5 mM CdCl₂) had an inner monolayer of hexadecanoic acid (C16:0) with two further layers of the 4:1 mixture of C18:1¹⁷ and C20:0 (A). The second (transferred from an aqueous subphase, pH 4.3, 20 dyn cm⁻¹, 1.5 mM CdCl₂) had an inner layer of nonadecanoic acid (C19:0), a middle layer of 4:1 C18:1¹⁷ and C20:0, and an outer layer of 4:1 21-docosenoic acid (C22:1²¹) and C20:0 (B). Hydrogenation of trilayer A for 173 min converted 23% of the total C18:1¹⁷ to C18:0. Hydrogenation of trilayer B for 5 min converted 49%

**Figure 9.** Turnover number, $N(\text{ML})$, vs. compressibility, C . Compressibility refers to monolayers at the air-water interface.

of the C18:1¹⁷ to C18:0, and 23% of the C22:1²¹ to C22:0. These experiments suggest that exchange of fatty acids between the layers of these supported multilayer films on platinum is a facile process.



Discussion

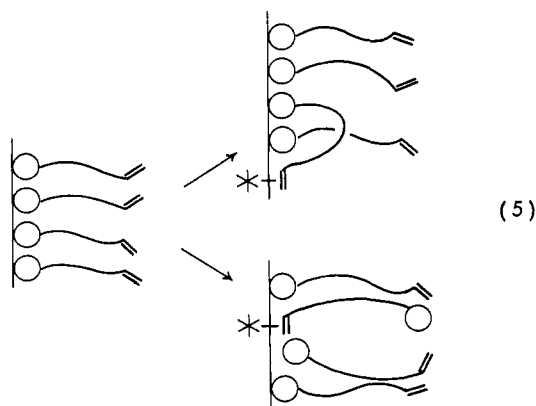
Supported monolayers of 17-octadecenoic acid (C18:1¹⁷), prepared by transfer of the oriented monolayer from an air-water interface to platinum, are reduced on exposure to dihydrogen. The rate of reduction depends on parameters which influence the structure of the monolayer, especially the pH and metal ion concentration of the aqueous subphase, and the surface pressure at which the film is transferred. The details of this dependence are relevant to examinations both of the structure of supported monolayer films and of the mechanisms of heterogeneous hydrogenation.

Structure of Monolayers Supported on Platinum. Two major factors seem to influence the rate of hydrogenation of the terminal double bond of C18:1¹⁷: the more important is the presence of catalyst poisons in the monolayer (especially cadmium ions and, perhaps, carboxylate groups); the less important is the rigidity of the film, as inferred from its compressibility at the A/W interface. Figure 9 plots the turnover numbers, $N(\text{ML})$, for hydrogenation of supported monolayers A–F (Table II) against the compressibility of the corresponding monolayers at the A/W interface (from Figure 6). The rate of hydrogenation of cadmium-containing monolayers is approximately 10^2 slower than that of calcium- or magnesium-containing monolayers of the same compressibility. This difference provides a measure of the poisoning effect of cadmium ion. Decreasing the compressibility within a series of related monolayers (A, A', and A'': D, E, and F) also decreases the rate. This observation suggests that hydrogenation proceeds more slowly in supported films derived from rigid monolayers at the A/W interface.

Two other observations suggest that the structure of the monolayers influences the rates of their reduction. First, the selectivity for internal and terminal double bonds is different for fatty acids incorporated into monolayers and for fatty esters in solution. Second, the rate of hydrogenation of fatty acids in monolayers is much slower than for 1-pentene over the same monolayer assemblies. Detailed interpretation of these observations is clouded by ambiguities: the phase homogeneity of the mixed films of internal and terminal fatty acids has not been established, and the uniformity of coverage of the platinum by the monolayers is not known. Nonetheless, both are compatible with the hypothesis that approach of the olefinic groups of a monolayer of unsaturated fatty acid to the platinum surface is hindered to a significant extent by its incorporation into the monolayer. Although the structure of the monolayer thus appears to exert a detectable influence on the reactivity of its component fatty acids, three observations suggest that the hydrocarbon portions of the monolayers considered in this work should be considered to have properties closer to viscous hydrocarbon liquids than to ordered, rigid crystals. First, the monolayer components do in fact experience sufficient motional freedom for the olefinic groups to reach the platinum surface and react. Second, fatty acids in the outer layers of certain trilayers also react. Third, external olefins diffuse through the monolayer to the platinum surface and hydrogenate with relatively little hindrance.

Two factors probably contribute to the fluidity of these organic films. First, the transfer pressures used in their preparation correspond, with the exception of monolayers A, A', and B', to liquid-condensed regions of the pressure-area isotherms. Second, the small but finite surface roughness of the platinum supports is such that accommodation of the film to the surface should result in a significant loss in structure. If we assume, for any of the pressure-area isotherms in Figure 6, that the monolayer is allowed to expand its area by 20–30% over that defined at the transfer pressure, the phase of the expanded monolayer would be gaseous. Since the surface area of the platinum foils is 20–30% greater than the area of the transferred monolayer, the real extent of expansion of the monolayer will be determined by its ability to cover the platinum surface uniformly. For the fluid monolayers assembled at low pH, this type of expansion seems plausible; for monolayers consisting of soap complexes or micelles, this expansion is more problematic.

The mechanism by which the double bond of the C18:1¹⁷ reaches the platinum surface prior to reduction is not established by the available evidence. The olefinic group may simply diffuse to the surface; alternatively, a more complex cooperative flipping of fatty acids may be involved (eq 5).⁸ In either



case, whatever restrictions imposed on the motion of the fatty acid chains by the order of the monolayer are not sufficient to prevent rapid contact of the terminal double bond with the surface.⁶⁹

The conclusions drawn from this work concerning the order and fluidity of supported monolayers seem to be in general agreement with those for lipid bilayers, for which surface pressures range from 10 to 35 dyn cm⁻¹.⁷⁰

Heterogeneous Hydrogenation. Hydrogenation of unsaturated monolayers on platinum clarifies the nature of the first cycles of heterogeneous catalytic hydrogenation. The observations that hydrogenation of C18:1¹⁷ proceeds with no induction period and that conditioning of the platinum foil with ethylene and dihydrogen before transfer of the monolayer has no influence on the hydrogenation kinetics bear on two problems. First, it has been suggested that catalytic hydrogenation takes place entirely on a carbonaceous overlayer.²¹ Although the importance of overlayers is documented in certain instances,^{22,57} it seems unlikely to be important in the system studied here: conversion of a significant fraction of the fatty acid monolayer to carbon would both reduce the yield of C18:0 and presumably obviate the requirement for added hydrogen. Further, an induction period might have been expected if a carbon layer were required. Second, the observation of a rapid reaction supports the classification of hydrogenation of simple olefins as a surface structure-insensitive reaction.⁴⁰ If only a small number of isolated sites on the surface were catalytically active, and if complete hydrogenation required appreciable lateral diffusion, the hydrogenation of the monolayer components might be expected to be slow or incomplete. Plots A''–F of Figure 5 suggest that surface diffusion, if any, is faster than reduction; the data of plots A and A' have been rationalized on the basis of slow exchange of olefins incorporated into slowly hydrogenated surface micelles with more rapidly reduced, nonmicellar, regions of the monolayer.

Experimental Section

General. NMR spectra were recorded on a Varian T-60 spectrometer using tetramethylsilane as a reference. Infrared spectra were recorded on a Perkin-Elmer Model 567 grating infrared spectrometer. Chemicals were obtained from the following sources and used as received: cadmium(II) chloride, carbon disulfide, cyclohexane, ethyl acetate, and magnesium(II) chloride from Mallinckrodt; hexadecanoic acid (C16:0), *trans*-9-hexadecenoic acid (C16:1^{9a}), octadecanoic acid (C18:0), and eicosanoic acid (C20:0) from Analabs or P-L Biochemicals Inc.; 21-docosenoic acid (C22:1²¹) was prepared by Dr. D. Bergbreiter;⁷² 1-hexene, 3,3-dimethyl-2-butene, cyclohexene, and cyclopentene from Aldrich; and dihydrogen and dioxygen from Middlesex Welding Supply Co., Cambridge, Mass. Platinum sheet (2 × 5 × 0.0002 or 0.004 in.) was purchased from Engelhard. Distilled water was purified by distillation from basic potassium permanganate solution through a 1-m vacuum-jacketed Widmer column. The pH of the water was adjusted with concentrated HCl, when required. The subphase pH was measured (±0.2) using narrow range pH strips (EM Laboratories, Elmsford, N.Y.). Chloroform (Mallinckrodt), used as a spreading solvent, was distilled under nitrogen through a 1-m vacuum-jacketed column packed with glass helices, and was used immediately. Typical concentrations used in spreading solutions were [C18:1¹⁷] = 4 mM, [C20:0] = 1 mM.

Ethyl 7-Hydroxyheptanoate. Cycloheptanone (45 g, 0.40 mol) was treated with an excess of trifluoroacetic acid according to the procedure of Smitsman et al.,⁷³ to yield 38 g (0.27 mol, 55%) of ethyl 7-hydroxyheptanoate: bp 110 °C (11 mm); IR (neat) 3400 (OH) and 1730 cm⁻¹ (C=O); NMR (CDCl₃) δ 4.1 (q, 2, J = 7 Hz), 3.5 (t, 2, J = 6 Hz, CH₂OH), 2.3 (t, 2, J = 6 Hz, OC(O)CH₂), 2.0–1.0 (m, 8, CH₂CH₂CH₂), and 1.2 (t, 3, J = 7 Hz).

Ethyl 7-Iodoheptanoate. Ethyl 7-hydroxyheptanoate (30 g, 0.17 mol) was converted to the corresponding tosylate.⁷⁴ The unpurified tosylate was dissolved in 500 mL of acetone and 51.6 g of sodium iodide (0.35 mol) was added according to the procedure of Tipson et al.⁷⁵ and stirred for 24 h to yield 29 g of ethyl 7-iodoheptanoate (0.10 mol, 60% based on starting alcohol); bp 80 °C (0.12 mm); IR (neat) 1730 cm⁻¹ (C=O); NMR (CDCl₃) δ 4.2 (q, 2, J = 8 Hz), 3.2 (t, 2, J = 6 Hz, CH₂), 2.4 (t, 2, J = 6 Hz, OC(O)CH₂), 2.0–1.0 (m, 8, CH₂CH₂CH₂), and 1.3 (t, 3, J = 8 Hz).

17-Octadecenoic Acid. The methyl cuprate of 11-chloroundecene (prepared from 11-hydroxyundecene according to the method of Hooz

and Gilani⁷⁶) was generated via its Grignard reagent and allowed to react with ethyl 7-iodoheptanoate.^{72,77} Copper(I) iodide (8.4 g, 44 mmol) was suspended in 80 mL of anhydrous THF in a 500-mL round-bottomed flask and cooled to -78°C . Methylolithium (21 mL of 2.07 M solution in ether, 44 mmol) was added; the suspension was stirred for 1 h, slowly warmed to 0°C , and cooled again to -78°C . An ether solution of 10-undecenyl-1-magnesium chloride (44 mmol, 49 mL of 0.90 M solution in THF) was added. The reaction mixture was stirred for 1 h at -78°C , warmed to -10°C , and cooled again to -78°C . Ethyl 7-iodoheptanoate (15 g, 53 mmol) and THF (20 mL) were added, the reaction mixture was allowed to stir at -78°C for 1 h and at room temperature for 2 h, and the reaction was ended by adding 50 mL of saturated aqueous NH_4Cl solution. The organic phase was separated and the aqueous phase extracted three times with an equal volume of ether. The organic phases were combined, washed with sodium chloride, dried over magnesium sulfate, and concentrated. The resulting oil was recrystallized from absolute ethanol. The product ester, ethyl 17-octadecenoate, was purified on a silica gel column by eluting with 5% ethyl acetate in cyclohexane. The yield of crude ester was 7.4 g (24 mmol, 54%); bp $125\text{--}129^{\circ}\text{C}$ (0.02 Torr); mp $25\text{--}27^{\circ}\text{C}$; IR (CCl_4) 1732 ($\text{C}=\text{O}$), 1638 cm^{-1} ($\text{C}=\text{C}$); NMR (CDCl_3) δ 6.2–4.8 (m, 3, $\text{CH}_2\text{CH}=\text{CH}_2$), 4.2 (q, 2, $J = 8$ Hz, $\text{CH}_3\text{CH}_2\text{O}$), and 1.2–2.6 (m, 33, $\text{CH}_2\text{CH}_2\text{CH}_2$, $\text{CH}_3\text{CH}_2\text{O}$, and $\text{OC}(\text{O})\text{CH}_2$). The ester (2 g, 6.5 mmol) was hydrolyzed by refluxing in 8 mL of 0.3 N sodium hydroxide for 24 h. The flask was cooled to room temperature and the resulting white solid separated by filtration and washed with distilled water. The solid was shaken with ether and water (pH 2.0) until the solid dissolved in the organic phase. The ether phase was separated and dried over magnesium sulfate. The ether was evaporated and the resulting solid recrystallized from wet methanol to yield 1.6 g of 17-octadecenoic acid (5.7 mmol, 88%); mp $55\text{--}55.5^{\circ}\text{C}$; NMR (CDCl_3) δ 11.7 (s, 1, COOH), 6.2–4.8 (m, 3, $\text{CH}=\text{CH}_2$), and 2.3–1.2 (m, 30, $\text{CH}_2\text{CH}_2\text{CH}_2$, $\text{CH}_2\text{CH}=\text{CH}_2$, and $\text{OC}(\text{O})\text{CH}_2\text{CH}_2$).

Anal. Calcd for $\text{C}_{18}\text{H}_{34}\text{O}_2$: C, 76.54; H, 12.13. Found: C, 76.39; H, 12.21.

Platinum Foils. The platinum foil monolayer supports ($2 \times 5 \times 0.004$ in. or 0.01 cm) were treated for 2 min with aqua regia at 50°C and rinsed with large quantities of distilled water. They were placed in a Vycor tube in a tube furnace and heated at 900°C in a slow stream of dioxygen for at least 24 h. The dioxygen was flushed from the tube with dinitrogen, and the foils were treated at 900°C with dihydrogen (until use, but at least 24 h). They were allowed to cool, and immediately transferred to the dipping trough. They were manipulated only with clean forceps, and exposure to the laboratory atmosphere before immersion in the dipping trough averaged 2 min. The foils could be reused after hydrogenation ca. 15 times by repeating the cleaning procedure. Eventually, the platinum developed visible crystallites and was deemed not suitable for further hydrogenation experiments.

Monolayer and Transfer Apparatus. A round Teflon trough with two motor-driven Teflon barriers was built based on the design of Fromherz.⁴⁵ Surface pressure was measured by the Wilhelmy method using a roughened mica plate attached to the balance arm of a Cahn ratio electrobalance, Model G. The electrobalance/Wilhelmy plate was zeroed and calibrated prior to monolayer formation with the plate suspended through the clean air–water interface. Room temperature pressure–area isotherms were measured point by point as the monolayers were compressed from the gaseous state at $0.01\text{ nm}^2\text{ molecule}^{-1}\text{ min}^{-1}$. The ferrite probe of a direct current displacement transducer (DCDT) (no. SS-101, G. L. Collins Corp., Long Beach, Calif.) was also attached to the balance arm. The transducer and probe were aligned by attaching the transducer to an X–Y translation stage connected to the base of the balance enclosure. The output of the DCDT is dependent on the position of the ferrite probe within the transducer, allowing for the monitoring of small movements of the balance arm. The DCDT output was coupled to the motor which moved the barriers and changed the surface area to compensate for any change in surface pressure. This system was sensitive to a surface-pressure variation of 0.10 dyn cm^{-1} . Monolayers were, therefore, transferred at constant surface pressure ($\pm 0.10\text{ dyn cm}^{-1}$) by lifting the platinum foil through the air–water interface via a motor-driven pulley at 1 cm/min. A typical transfer curve is shown in Figure 10. The apparatus was enclosed in a laminar air-flow hood which kept particulate matter from accumulating. During an experiment, the air flow was discontinued to eliminate vibration and the effects of rapid air movement. The apparatus was placed on a table designed to

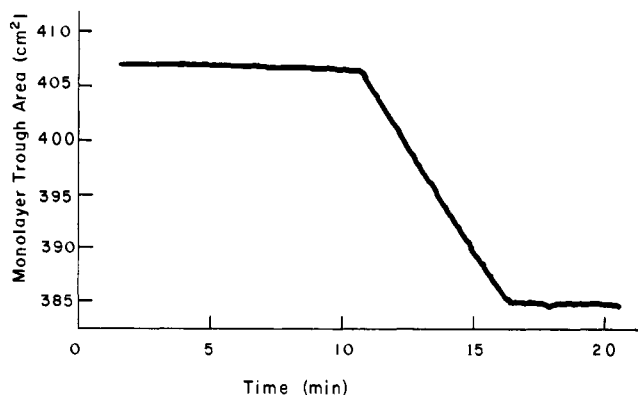


Figure 10. Plot of the area of an oriented monolayer film at the A/W interface as a function of time during transfer to a platinum foil having a geometrical surface area of 23 cm^2 . The difference between the two plateaus (23 cm^2) represents the area of film transferred to the foil. The slope of the plateau indicates the rate of collapse or solution of the monolayer (in this instance negligible).

minimize the effects of building vibrations.

Monolayer Preparation, Hydrogenation, and Analysis. The surface of the aqueous subphase was swept several times with the barrier arms to remove surface active impurities. A platinum foil was attached to a pulley and lowered beneath the surface of the subphase. The spreading solution containing fatty acids ($50\text{ }\mu\text{L}$, ca. 5 mM) was placed on the surface, and the chloroform allowed to evaporate (5 min). The monolayer was compressed to the required surface pressure. The foil was withdrawn through the air–water interface ($4\text{ cm}^2\text{ min}^{-1}$). During withdrawal, the meniscus was inspected closely visually; foils in which the meniscus moved down the plate inconsistently were considered to be dirty, and discarded. The monolayer covered foils appeared to be dry when they emerged from the subphase. They were immediately suspended in a 500-mL Fischer-Porter hydrogenation bottle fitted with a pressure gauge, vent, and hydrogen inlet. Hydrogen was continuously passed through the reaction vessel for the desired reaction time at ca. 50 mL min^{-1} . All hydrogenations were carried out at atmospheric pressure and room temperature. At the end of the allotted reaction time the foil was removed and suspended over concentrated HCl for 5 min. The foil was rinsed with 0.5 mL of CHCl_3 into a funnel fitted with a drain and stopcock. The chloroform solution was transferred to a 1-mL round-bottomed flask and the solvent removed by distillation. The flask was cooled to room temperature and 0.5 mL of freshly distilled diazomethane–ether was added.⁷⁸

The excess diazomethane–ether was removed by distillation after a 10-min reaction time. To the residue was added $10\text{ }\mu\text{L}$ of CS_2 solution containing 0.64 mM methyl palmitate and $15\text{ }\mu\text{L}$ of CS_2 solution containing 0.75 mM methyl behenate; the final volume was $25\text{ }\mu\text{L}$. Analyses were performed by GLC at 190°C on a $6\text{ ft} \times \frac{1}{8}$ in. stainless steel column (Applied Science) packed with 10% Apolar 10-C on 100/120 Gas Chrom Q. Peak areas were measured electronically on a Spectra-Physics Minigrater.

Hydrogenation of Olefins Present in the Vapor Phase. The foils used in these experiments underwent the same cleaning procedure as those used for monolayer hydrogenations. The monolayers transferred to these foils were identical with those used to determine the kinetics of monolayer hydrogenation. The foil was placed in a 500-mL Fischer-Porter hydrogenation bottle. The system was charged with dihydrogen (1300 Torr) and a mixture of 1-pentene and cyclohexane (4:1, 0.20 mL). The hydrocarbons vaporized completely within 20 s to give a pressure rise of 100 Torr. The vapor was mechanically agitated throughout the course of the hydrogenation. The reaction was followed by periodically withdrawing 2 mL of the vapor in a gas-tight syringe. The extent of hydrogenation was determined by GLC ($6\text{ ft} \times \frac{1}{8}$ in. aluminum column, packed with 15% tris(cyanoethoxy)propane on 80/90 F-1 alumina; 51°C) using the cyclohexane as internal standard.

Competitive hydrogenations were carried out in analogous fashion using mixtures of two olefins and an internal standard.

Multilayer Hydrogenation. Multilayers were prepared by repetitively dipping and withdrawing a clean platinum foil through the monolayer covered interface. The initial monolayer (C16:0, pH 5.6,

1.5 mM CdCl₂, 20 dyn cm⁻¹, A, and C19:0, pH 4.3, 1.5 mM CdCl₂, 20 dyn cm⁻¹, B) transferred to the foil upon raising it through the A/W interface. The foils were hydrophobic indicating that the fatty acid was oriented with the carboxyl group at the platinum surface. This monolayer was then removed from the aqueous surface. The fatty acids used for the second layer (4:1 mixture of C18:1¹⁷ and C20:0, A and B) were spread and compressed to 20 dyn cm⁻¹. This monolayer was transferred upon lowering the foils through the A/W interface. The foils were now hydrophilic indicating that the carboxyl groups were oriented away from the platinum surface. The third layer of the first trilayer (4:1 mixture of C18:1¹⁷ and C20:0, A) was transferred by again raising the foil through the A/W interface. For the second trilayer (B), the aqueous surface was cleaned after transferring the second layer. The fatty acids used for the third layer (4:1 mixture of C22:1²¹ and C20:0, pH 5.6, 1.5 mM CdCl₂, 20 dyn cm⁻¹) were spread and compressed. This was transferred upon raising the foil through the A/W interface. The first trilayer was exposed to dihydrogen (1 atm) for 173 min and the second for 5 min. Analyses were performed as for the other monolayer experiments.

Monolayer Hydrogenation on Ethylene-Pretreated Platinum. Clean platinum foils were treated with a mixture of ethylene (57 Torr) and dihydrogen (1300 Torr) for 10 min. The foils were hydrophilic after this treatment and subsequent exposure to air. Monolayers of a 4:1 mixture of C18:1¹⁷ and C20:0 were transferred (pH 5.6, no ions) and exposed to dihydrogen in the usual manner.

Pressure Dependence of Monolayer Hydrogenation. Monolayers of a 4:1 mixture of C18:1¹⁷ and C20:0 were spread (pH 5.6, 1.5 mM MgCl₂, 20 dyn cm⁻¹) and transferred to clean platinum foils. The hydrogenations were carried out under a total N₂ plus H₂ pressure of 1300 Torr. The partial pressure of hydrogen was varied from 100 to 1300 Torr. The reaction time was held constant. Analysis of the extent of hydrogenation was performed in the usual manner. The conversion of C18:1¹⁷ to C18:0 did not vary within the experimental error ($\pm 10\%$) over this dihydrogen pressure range.

Hydrogenation of the Methyl Esters of C18:1¹⁷ and C16:1^{9t} in Ethyl Acetate. One milligram of PtO (Engelhard Industries) was added to 2 mL of ethyl acetate. The stirred suspension was deoxygenated with argon. The PtO was reduced by exposure to dihydrogen for 15 min. An ethyl acetate solution (2 mL) of methyl C18:1¹⁷ (14.8 mM) and methyl C16:1^{9t} (15.5 mM) was added to the Pt(0) suspension. The hydrogenation was carried out under dihydrogen at 1 atm. Aliquots (0.1 mL) were removed and added to 0.05 mL of carbon disulfide. The carbon disulfide poisons the catalyst and quenches the hydrogenation reaction. The rates of conversion of methyl C18:1¹⁷ and methyl C16:1^{9t} to C18:0 and C16:0 were determined by GLC at 190 °C on a 6 ft \times 1/8 in. stainless steel column (Applied Science Laboratories) packed with 10% Apolar 10-C on 100/120 Gas Chrom Q. Doubling the dihydrogen pressure had no effect on the rate of hydrogenation.

Electrochemistry. The cyclic voltammogram for a platinum foil electrode was measured on a Princeton Applied Research Model 174A polarographic analyzer and recorded on an Omnigraphic 2000 X-Y recorder. The polarographic analyzer was capable of only single sweep voltammetry, but by manually reversing the sweep direction it was possible to generate cyclic voltammograms. The electrolyte (1 M HClO₄) was deoxygenated with N₂ through a gas dispersion frit for a minimum of 30 min prior to use and measurements were carried out under N₂. The cell consisted of three compartments containing, respectively, a saturated calomel reference electrode (SCE), platinum foil working electrode, and platinum wire counter electrode.⁷⁹ Electrochemically active species present in the cell which could have interfered with subsequent experiments were removed by alternate potentiostatic oxidation and reduction at 1.5 and -0.3 V, respectively, using a Princeton Applied Research Model 371 potentiostat-galvanostat.

A distinction should be made between experiments involving electrochemically cleaned and repetitively electrochemically cycled platinum samples. The hydrogenation of monolayers on an electrochemically cleaned foil necessitated the use of large foils (2 \times 5 \times 0.004 in). The use of these foils as the working electrode leads to currents above 50 mA at oxidizing potentials and below -50 mA at reducing potentials. The PAR Model 174A polarographic analyzer was only capable of operating at currents above -10 mA and below 10 mA. It was, therefore, necessary to cut small samples (ca. 1 cm²) from the larger platinum foils in order to generate correspondingly smaller currents. The platinum foil working electrodes used to gen-

erate the cyclic voltammograms in Figures 1B and 1C were cleaned by repetitive electrochemical cycling (at least ten cycles) between 1.3 and -0.2 V at 200 mV s⁻¹.

Electron Microscopy. Platinum foil samples (5 \times 5 \times 0.05 mm) for electron microscopy underwent the same treatment as those used as monolayer supports. The oxidized surfaces (Figure 3) were removed from the heat treatment chamber prior to the introduction of nitrogen. All electrochemically treated samples were cycled five times from 1.3 to -0.2 V (vs. SCE, 200 mV s⁻¹, 1 M HClO₄, 25 °C), rinsed with distilled water, and allowed to dry in air. The samples were attached to the sample holder with double-faced electrically conducting copper tape. The scanning electron microscopy was done on a Cambridge Steroscan Mark 2A (Cambridge, England). The X-ray emission spectra for SEM samples could be routinely measured (Kevex-Ray, Burlingame, Calif.). The only heavy element detected for the oxidized, reduced, and monolayer coated foils was platinum. X-ray emissions are not detectable for the lighter elements (C, O). The surface concentration of Mg and Cd on foils coated with monolayers containing these elements was too low to be detected by X-ray emission. ESCA analysis (Hewlett-Packard ESCA Spectrometer System 5950A, Palo Alto, Calif.) of clean platinum foils indicated the presence of Pt, C, and O. Magnesium and cadmium were detectable on foils coated with monolayers containing these elements.

A fully treated platinum foil surface was replicated by applying 3 drops of 1% Parlodion in amyl acetate (Tousimis Research Corp., Rockville, Md.) to the surface. A copper grid (2.3 mm diameter, 300 mesh; Polaron Inst., Inc., Warrington, Pa.) was sandwiched between the replica and the adhesive tape and the replica was removed from the foil surface by lifting the adhesive tape. The grid, which was covered with the replica, was removed from the adhesive tape and placed in the vacuum chamber of a CVC evaporator (Consolidated Vacuum Corp., Rochester, N.Y.). A layer of chromium (~ 200 Å) was deposited at a 32° incidence angle from a resistively heated chromium wire. The replica was examined (Figure 3) under a JEM-7 electron microscope (Japan Electron Lab. Co.). Efforts to replicate monolayer coated platinum surfaces in a similar manner were unsuccessful since the dried Parlodion film could not be lifted from the surface.

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- (66) The equilibrium spreading pressure as used here indicates the surface pressure of a monolayer in the gaseous state. The value of Π_{eq} was measured by extrapolating the nearly horizontal gaseous region of the pressure-area isotherm (Figure 6) to zero area per molecule.
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