

Adsorption and Hydrogenolysis of Cyclopropanecarboxylic Acid on Aluminum Oxide

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Abstract: The temperature- and exposure-dependent interaction of cyclopropanecarboxylic acid with alumina surfaces has been studied with inelastic electron tunneling spectroscopy. Cyclopropanecarboxylate and *n*-butyrate were the only adsorbed species formed, as determined by a comparison with tunneling spectra of *n*-butyric acid and cyclopropanecarboxylic acid coadsorbed on alumina. The *n*-butyrate results from hydrogenolysis of the cyclopropyl ring of the adsorbed cyclopropanecarboxylate, with the hydrogen supplied by surface hydroxyl groups. The relative populations of the two surface species are strongly dependent upon coverage and temperature.

1. Introduction

Tunneling spectroscopy has been employed to characterize a variety of surface reactions from the chemisorption of carboxylic acids on Al_2O_3 ¹⁻⁶ to the reaction of acetylene with the polymerization catalyst $\text{Zr}(\text{BH}_4)_4$ supported on Al_2O_3 .⁷ Tunneling spectroscopy has several advantages over conventional infrared spectroscopy when applied to these systems. Among these advantages are submonolayer sensitivity in connection with low area surfaces, a large electron-vibration cross section for carbon-hydrogen modes, the observation both of dipolar and induced dipolar modes, and an excellent vibrational window extending below 250 cm^{-1} .

In this study, tunneling spectroscopy is used to examine the adsorption and hydrogenolysis of cyclopropanecarboxylic acid ($\text{C}_3\text{H}_5\text{COOH}$) on alumina. Molecular carboxylic acid adsorbs dissociatively on alumina, resulting in an adspecies that is bound to the surface through the two carboxylate oxygen atoms as the symmetrical, bidentate cyclopropanecarboxylate ion, probably of the bridging rather than the chelating type.² Consequently, for cyclopropanecarboxylic acid, the surface bond through the carboxylate moiety serves to constrain the three-membered ring in close proximity to the surface, allowing subsequent reaction and/or fragmentation. In this way, $\text{C}_3\text{H}_5\text{COOH}$ affords the opportunity to study the interaction of a strained ring having properties similar to unsaturated π -electron systems⁸ with the Al_2O_3 surface.

In a similar manner, unsaturated carboxylic acids adsorbed on alumina have been used to study the hydrogenation of carbon-carbon multiple bonds by the alumina surface. McBride and Hall⁹ advantageously used muconic acid ($\text{HOOC}-\text{HC}=\text{CH}-\text{HC}=\text{CH}-\text{COOH}$) to study the hydrogenation of carbon-carbon double bonds on plasma-grown Al_2O_3 by tunneling spectroscopy. Similarly, Jaklevic¹⁰ studied the hydrogenation of the carbon-carbon triple bond of propiolic acid ($\text{HC}\equiv\text{CCOOH}$) by tunneling spectroscopy. Unlike these simple hydrogenation reactions, however, adsorbed cyclopropanecarboxylic acid undergoes a skeletal rearrangement that involves the breaking of a carbon-carbon bond.

Evidently, there has been no prior work concerning the adsorption or reaction of $\text{C}_3\text{H}_5\text{COOH}$ with Al_2O_3 . However, γ - Al_2O_3 (dehydroxylated at 723 K in vacuo) catalyzes the exchange

between D_2 and various alkanes, including cyclopropane and methylcyclopropane, at temperatures as low as 250 K.¹¹ On the other hand, the rates of γ - Al_2O_3 catalyzed isomerization of cyclopropane to propene and methylcyclopropane to *trans*-2-butene were measurable only above 335 K.¹¹ Note that exchange and isomerization are thought to be catalyzed by different active sites.¹² Although the isomerization of methylcyclopropane over SiO_2 - Al_2O_3 also produced strictly *n*-butenes,¹³ the isomerization mechanisms over SiO_2 - Al_2O_3 and Al_2O_3 are probably quite different, the former proceeding via a carbenium ion intermediate¹³ and the latter proceeding via a carbanion intermediate.^{11,12} In contrast, thermal cracking of methylcyclopropane yields a nearly uniform distribution of structural isomers and is thought to proceed via radical intermediates.¹⁴ Although alumina is not normally thought to be a hydrogenation catalyst, pure γ - Al_2O_3 (dehydroxylated at 923 K in vacuo) is active for the hydrogenation of adsorbed ethylene,¹⁵ and a composite Al_2O_3 consisting of γ - Al_2O_3 and bohemite (AlOOH) is active for the hydrogenation and isomerization of pent-1-ene.¹⁶ Although hydrogenolysis of cyclopropane and alkylcyclopropanes is observed in catalytic hydrocracking, the catalysts used in hydrocracking combine metal centers for catalytic hydrogenation on a SiO_2 - Al_2O_3 support that functions for isomerization and catalytic cracking.^{17,18} However, it should be noted that while *n*-butane is the only observed product in ring-opening hydrogenolysis of methylcyclopropane over SiO_2 - Al_2O_3 supported platinum, isobutane (94-97%) is the product over SiO_2 supported platinum.¹⁹

The major results presented here are the identification of two stable intermediates in the reaction of cyclopropanecarboxylic acid with a plasma-grown aluminum oxide surface and a characterization of the reactivity pattern of the oxide for this particular reaction. For cyclopropanecarboxylic acid, adsorption initially results in the formation of the cyclopropanecarboxylate surface species. This species may interact with surface hydroxyls to form a new surface species, an *n*-butyrate, by hydrogenolysis of the cyclopropyl ring. The hydrogenolysis reaction is more likely to take place at room temperature if the coverage of the cyclopropanecarboxylate is low, thereby maximizing the number of

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available hydroxyls per adsorbed cyclopropanecarboxylate, or on an alumina surface that is heated above 500 K, thereby mobilizing the surface hydrogen.

To demonstrate the above ideas, the paper proceeds as follows. Section 2 puts forth experimental details and tunnel junction fabrication procedures. Section 3 identifies the adsorbed cyclopropanecarboxylate as the principal chemisorbed species formed when the plasma-grown alumina is exposed to 0.4 torr-s of cyclopropanecarboxylic acid at 295 K. Here, the identification is by means of a comparison between the tunneling spectrum of the surface species and optical spectra of the sodium salt of cyclopropanecarboxylic acid. In section 4 it is shown that cyclopropanecarboxylic acid can form a second surface species, the *n*-butyrate adspecies, upon adsorption and reaction with the aluminum oxide. This is done by a comparison of two tunneling spectra, one of which was prepared by heating the alumina to 550 K during exposure to cyclopropanecarboxylic acid and the other by exposing the alumina at 295 K to both cyclopropanecarboxylic acid and *n*-butyric acid vapors. As noted above, the cyclopropanecarboxylate species is unstable on the alumina surface at temperatures above 500 K and reacts to form the *n*-butyrate. Hence, the alumina heated to 550 K while exposed to the cyclopropane acid should show a larger fraction of the *n*-butyrate in its total adspecies population. Similarly, when *n*-butyric acid and cyclopropanecarboxylic acid are coadsorbed on Al_2O_3 at 295 K, the relative population of the *n*-butyrate species is "artificially" increased. Tunneling spectra of these two junctions should be very similar if *n*-butyrate is indeed the reacted form of the cyclopropanecarboxylate. In section 5, the mechanism of the surface reaction is discussed. Isotopic labeling experiments are analyzed for information pertinent to these two topics. Finally, the paper is concluded with a summary in section 6.

2. Experimental Procedures

The cyclopropanecarboxylic acid (95% purity), the *n*-butyric acid ($\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$) (>99%), the isobutyric acid [$(\text{CH}_3)_2\text{CHCOOH}$] (>99%), and deuterium oxide (D_2O) (>99%) were obtained from Aldrich Chemical and were used without further purification. Deuterium-labeled cyclopropanecarboxylic acid ($\text{C}_3\text{H}_5\text{COOD}$) was synthesized from the unlabeled reagent by an acid-catalyzed exchange with D_2O : 5 mL of $\text{C}_3\text{H}_5\text{COOH}$, 5 mL of D_2O , and one drop of HCl were mixed and allowed to equilibrate for 30 min in a water bath at 30 °C. The mixture was vacuum distilled to leave the deuterium-enriched cyclopropanecarboxylic acid. This sequence was repeated three additional times using the deuterium-enriched cyclopropanecarboxylic acid from the previous sequence as the starting material for the current sequence. An NMR spectrum of the final product showed that the deuterium enrichment of the acid proton was greater than 99%. In addition, the IR spectrum showed no absorption at 1178 cm^{-1} , indicating that the residual concentration of D_2O was negligible.

Typically, junction fabrication was begun by the evaporation of 800 Å of an aluminum film from a tungsten coil through a mask onto a borosilicate glass substrate 2.5 cm × 1 cm × 1 mm in dimension. The base pressure prior to evaporation was below 1×10^{-8} torr, and the film thickness was monitored by a quartz crystal microbalance. The aluminum film was annealed by resistive heating. The temperature was correlated with the film resistance, and, following Bowser and Weinberg,²⁰ this technique was used to control the substrate temperature in all subsequent steps in the synthesis of the junction. A cohesive oxide was then grown on the aluminum film by an oxygen plasma discharge. To grow a suitable oxide barrier in the UHV environment, traces of water were required in the oxygen plasma atmosphere. [Brown and Walmsley³ have also noted problems with rigorously dried O_2 .] Pumpdown was followed by exposure to the adsorbate from the vapor phase. During this step, the oxide temperature was controlled as described above, and the pressure was monitored by Varian UHV or Millitorr ionization gauges. In some cases, the oxide was maintained at room temperature during exposure and then heated following the evacuation of the bell jar. For the cyclopropanecarboxylic acid, typical pressures during exposure were between 0.1 and 0.5 μ .

After exposure to the adsorbate, 2000 Å of lead was evaporated at a pressure below 1×10^{-5} torr, in a cross-strip pattern to form the completed junction. Junctions were removed from the vacuum system and

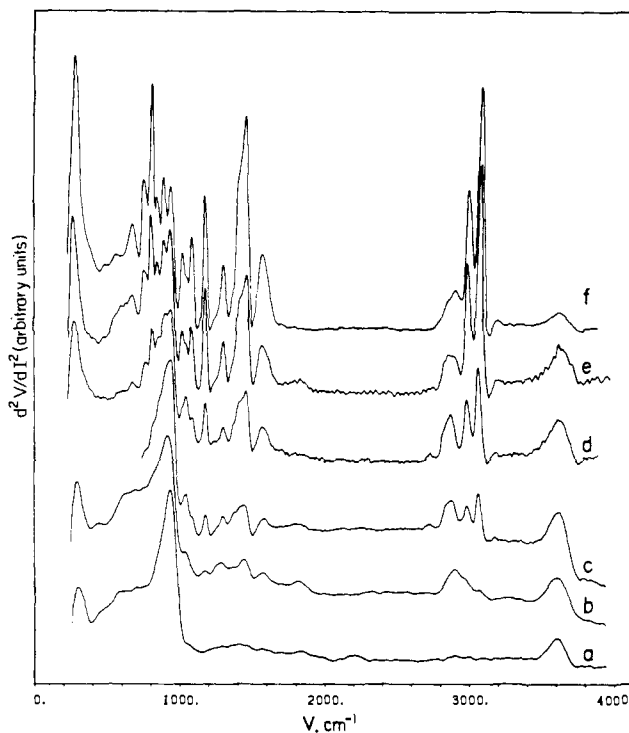


Figure 1. Inelastic electron tunneling spectra of alumina at 295 K exposed to increasing fluxes of cyclopropanecarboxylic acid vapor: (a) clean Al_2O_3 surface, (b) 0.025 torr-s, (c) 0.05 torr-s, (d) 0.1 torr-s, (e) 0.2 torr-s, and (f) 0.4 torr-s.

mounted for immersion in liquid helium. All measurements were carried out at 4.2 K with PDP 11/10 digitally controlled electrons.²¹ The spectra were accumulated through multiple scan averaging, typically on the order of several hundred separate scans. The data were then processed as follows: (1) the spectra were first smoothed by a cubic convolute;²² (2) an attempt was made at background removal (only linear functions of voltage were used to fit the background); (3) the peaks were located by a least-squares fit of the first derivative, followed by an interpolated location of the first-derivative zero crossings; and (4) peak energies were corrected for the lead superconducting band gap and for modulation effects on the band gap width.²³

For the isotopic labeling experiments, special procedures were required to produce a fully deuterated alumina surface. Since surface hydroxyls exchange rapidly with D_2O or H_2O vapor, it was necessary to exchange the H_2O in the bell jar completely with D_2O . This was done by heating the bell jar to 75 °C and then performing three successive cycles of evacuation to 10^{-5} torr and exposure to several torr of D_2O vapor for approximately 1 h. A quadrupole mass spectrometer monitored the residual gas spectrum in the bell jar, and the degree of isotopic exchange could be evaluated from the ratio of mass peaks 20 (D_2O) to 19 (HDO). Following the third exposure to D_2O vapor, the bell jar was cooled and evacuated to approximately 1×10^{-7} torr, and the aluminum evaporation was performed. The molar ratio of D_2O to HDO was greater than 7:1 at this point. For the plasma oxidation, an $\text{O}_2/\text{D}_2\text{O}$ mixture was used, but following the plasma oxidation, the D_2O to HDO ratio decreased slightly. To ensure nearly complete exchange of deuterium groups for hydroxyl groups, the alumina surfaces were subjected to a high-pressure "beam dose" of D_2O vapor. From this point, the tunnel junctions were completed in the conventional manner described above.

The infrared sample was prepared by spraying a CaF_2 disk with Degussa Aluminum Oxide C, following the procedures of Yang and Garland.²⁴ The IR cell was evacuated and exposed to approximately 300 μ of $\text{C}_3\text{H}_5\text{COOH}$ for 500 s at room temperature, and then evacuated for several hours.

3. Cyclopropanecarboxylate Surface Species

A peak-by-peak comparison of the modes in the tunneling spectrum of Figure 1f below 2000 cm^{-1} shows excellent agreement

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Table I

C ₃ H ₅ COO ⁻ approx assignments	C ₃ H ₅ COO ⁻ Na ⁺ Maillols IR/Raman	IETS		<i>n</i> -C ₃ H ₇ COOH/Al ₂ O ₃		<i>n</i> -C ₃ H ₇ COO ⁻ approx assignments
		295 K, 0.4 torr-s	IETS 550 K, 0.4 torr-s	IETS 300 K		
A'' ν _a (CH ₂)	3100/3095					
A' ν _a (CH ₂)	.../3083	3084	3084			
A'' ν _s (CH ₂)	3050/3048					
A' ν _s (CH ₂), ν(CH)	3015/3018	3003	3005			
		2840-2920* (sh)		2962	2942	ν _a (CH ₃)
		1830		2908	2904	ν _a (CH ₂)
		1582		2970-2960 (sh)	2861	ν _s (CH ₂), ν _s (CH ₃)
ν _a (CO ₂ ⁻)	1555/1537	1470	1470 (sh)	1588	1583	ν _a (CO ₂ ⁻)
ν _s (CO ₂ ⁻)		1440-1450 (sh)	+	1450	1448	δ _s (CH ₂), δ _a (CH ₃)
δ _s (CH ₂)	1445/1453					δ _s (CH ₂), ν _s (CO ₂ ⁻)
ν _s (CO ₂ ⁻)	1418/1429					
A'' τ(CH ₂)	1305/1309	1317	1309	1382	1375	δ _s (CH ₃)
				1258	1297	
					1256	δCH ₂ progression
					1200	
A' τ(CH ₂)	1225/1232 (f)					
ring breathing	1190/1198	1186	1187			
ν(C-COO ⁻)	1083-1090/1095	1092	+	1091	1082	
			+	1051	1044	ν(C-C)
A' w(CH ₂)	1040/1034	1034				
A'' w(CH ₂)	.../1020	1026				
ring deformation	945/946	951	940-960 (sh)			
A'' ρ(CH ₂)	910/914	901	901			
					892	ρ(CH ₃)
					872	
A' ρ(CH ₂)	850/853	855	862			
ring deformation	820/826	816	818			
δ(1-CH) out of plane	.../791					
δ _s (CO ₂ ⁻)	758/772	764				
δ(1-CH) in plane	648/645	690				
w(CO ₂ ⁻)	.../550			652	670	
ρ(CO ₂ ⁻)	.../492					
τ(C-CO ₂ ⁻)	285/282	294	+	290	290	

with the IR and Raman spectroscopic data of Maillols²⁵ for sodium cyclopropanecarboxylate (see Table I). This suggests that under the conditions of Figure 1f (295 K and 0.4 torr-s exposure), cyclopropanecarboxylic acid adsorbs on the plasma-grown Al₂O₃ predominantly as the cyclopropanecarboxylate anion. This is consistent with nearly all investigations of the chemisorption of carboxylic acids on Al₂O₃ surfaces to date, where it has been concluded that the initially adsorbed species is the carboxylate anion of the acid. Using Raman depolarization, Maillols²⁵ identified mode symmetries, and, aided by theoretical and gas-phase spectra of cyclopropane and its derivatives, proposed consistent mode assignments.

A tunneling spectrum of the clean alumina surface is shown in Figure 1a. This spectrum shows characteristic modes at 3600 cm⁻¹ (due to the surface O-H stretching vibration) and at 940 and 650 cm⁻¹ (due to bulk Al-O vibrations). If the clean alumina surface is exposed to increasing fluxes of cyclopropanecarboxylic acid, then Figure 1b through 1f result, with Figure 1f being a near-saturation exposure.

The point group symmetry for the free cyclopropanecarboxylate anion is C_s. The symmetry element is the plane, that is, perpendicular to the plane containing the cyclopropyl ring and which bisects the cyclopropyl ring through the tertiary carbon center. In the gaseous carboxylic acid, the O=C-OH group lies entirely in the symmetry plane.²⁶ Maillols²⁵ was able to assign 24 of the 27 vibrational modes of the free anion. The modes that were not assigned correspond to the A'' CH₂ scissoring mode [A'' δ_s(CH₂)], and two deformation modes [A' and A'' δ(C-C)]. The similarity between the tunneling spectra and the IR and Raman spectra has made it possible to confidently assign nearly 24 vibrational modes of the adsorbed species in direct analogy. From the close cor-

respondence between the CH₂ stretching and deformation modes in the free anion and in the adsorbed species, it is apparent that the C_s symmetry classification is also valid for the CH₂ groups on the cyclopropyl ring of the adsorbed species. In addition to the 27 free anion vibrational modes, six additional modes—three frustrated translations and three frustrated rotations—are expected at low frequencies for the cyclopropanecarboxylate adsorbed on Al₂O₃. These modes are associated with deformation and stretching vibrations of Al-O-type bonds, and hence, in view of the strong vibrational peaks from the Al-O modes of the alumina barrier, are extremely difficult to detect. Thus, the six additional modes cannot be assigned with confidence, but this does not mitigate against any of the arguments to be made subsequently. As mentioned above, the adsorbate spectrum is almost, but not completely analogous to the free carboxylate anion spectrum. Hence, there are a number of mode assignments which shall be discussed individually.

3.1. Spectral Modes below 800 cm⁻¹. For a surface acetate species, identified as the adsorbed species after acetic acid chemisorption on Al₂O₃, the COO⁻ rocking, wagging, and scissoring modes appear as well-defined peaks of weak to moderate intensity near 475, 610, and 680 cm⁻¹, respectively.² The adsorption of propenoic acid (CH₂=CHCOOH) on Al₂O₃ results in a surface species with low-frequency modes at 511, 630, and 684 cm⁻¹.⁴ To be consistent with these data, it is necessary to assign the peaks in Figure 1f at 490, 565, and 680 cm⁻¹ to the COO⁻ rocking [ρ(COO⁻)], the COO⁻ wagging [ω(COO⁻)], and the COO⁻ scissoring (δ_s(COO⁻)) modes, respectively (cf. Table I).²⁷ The in-plane CH deformation mode [A' δ(CH)] is assigned as the peak at 764 cm⁻¹. This switches Maillols' assignment²⁵ of the COO⁻ scissoring mode and the in-plane CH deformation mode.

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Our proposed assignment, however, is more consistent with the observed line shapes. The COO^- rocking, wagging, and scissoring modes are observed to be broad and weak. There are two possible effects responsible for this: (1) *lifetime broadening* of the modes since vibrational energy transfer to the substrate lattice may be rapid for bonds adjacent to the surface; and (2) since the cyclopropanecarboxylate anion is chemisorbed through the carboxylate oxygen atoms, the COO^- wagging, twisting, and rocking modes would be especially sensitive to *adsorption site heterogeneity*. On the other hand, for the CH in-plane deformation mode there is no a priori reason for expecting peak broadening or shifting, and the intensity and sharpness of the peak at 764 cm^{-1} are consistent with this.

3.2. Spectral Mode near 950 cm^{-1} . It is logical to associate the peak at 951 cm^{-1} in the tunneling spectrum with the ring deformation mode observed at $945/946\text{ cm}^{-1}$ (IR/Raman) by Maillols.²⁵ However, electron coupling to Al–O longitudinal stretching modes contributes additional energy losses near this frequency. In junctions without an adsorbate on the oxide surface, this coupling yields a broad, intense peak characteristic of the tunneling spectrum of the Al_2O_3 barrier (cf. Figure 1a). This peak appears consistently in our unheated Al_2O_3 barriers at approximately 940 cm^{-1} . Traditionally, this Al–O mode assignment follows from polarized IR studies of electrochemically grown Al_2O_3 .²⁸ The observation by De Cheveigne et al.⁶ concerning the sensitivity in the Al–O longitudinal phonon mode to perturbations by ^{18}O isotopically labeled carboxylic acid adsorbates indicates that the Al–O bonds of the adsorbate–surface complex furnish a significant fraction of the peak intensity of the Al–O mode. The 945-cm^{-1} ring deformation mode is intensely IR active, and the sharp adsorbate peak appears superposed on the broad Al–O band. This implies that the $951\text{- and }901\text{-cm}^{-1}$ peaks [due to the A'' $\nu(\text{CH}_2)$ modes] are shifted down and up, respectively, in frequency from their true, deconvoluted values. As a consequence, the frequencies observed in tunneling spectroscopy are shifted slightly further from the spectroscopic data for the free anion.

3.3. A' $\delta(\text{CH}_2)$ and $\nu_s(\text{COO}^-)$ Modes. The assignment of the symmetric COO^- stretching mode [$\nu_s(\text{COO}^-)$], the CH_2 scissoring (symmetrical in-plane deformation) mode [$\delta_s(\text{CH}_2)$], and the CH_3 asymmetric deformation mode [$\delta_a(\text{CH}_3)$] in carboxylic acids adsorbed on Al_2O_3 has been disputed in the literature. Recently with $\text{CH}_3\text{C}^{18}\text{O}^{18}\text{OH}$, De Cheveigne et al.⁶ have established firmly, however, the identification of the $\nu_s(\text{COO}^-)$ mode at 1470 cm^{-1} in the acetate adspecies. In the adsorbed cyclopropanecarboxylic acid, the symmetric COO^- stretching mode and the CH_2 scissoring mode appear as a very strong peak at 1470 cm^{-1} , with a prominent low-frequency shoulder (Figure 1f). Analogy with the acetate adspecies suggests that the 1470-cm^{-1} peak in the spectrum of adsorbed $\text{C}_3\text{H}_5\text{COOH}$ is due to the $\nu_s(\text{COO}^-)$ vibrational mode, and the low-frequency shoulder results from the CH_2 scissoring mode. Without performing a detailed (and not unambiguous) peak deconvolution, an estimate of 1450 cm^{-1} is deduced for the vibrational frequency of the CH_2 scissoring mode that gives rise to the shoulder. This frequency correlates well with the A' $\delta_s(\text{CH}_2)$ mode of the cyclopropanecarboxylate sodium salt observed by Maillols at 1445 and 1453 cm^{-1} in the IR and Raman spectra, respectively.²⁵

Shifts in the COO^- asymmetric and symmetric stretching frequencies of the adsorbed carboxylate from the corresponding sodium salt frequencies imply much about bonding between the carboxylate and the surface. For cyclopropanecarboxylate, the $\nu_s(\text{COO}^-)$ and $\nu_a(\text{COO}^-)$ modes are upshifted from 1429 and 1537 cm^{-1} in the Raman spectrum of the sodium salt to 1470 and 1582 cm^{-1} in the tunneling spectrum: shifts of $+41$ and $+45\text{ cm}^{-1}$, respectively. This is comparable to shifts in the acetate adspecies on Al_2O_3 . The $\nu_s(\text{COO}^-)$ and $\nu_a(\text{COO}^-)$ modes in the acetate anion shift from 1413 and 1556 cm^{-1} (Raman spectrum of the sodium salt²⁹) to 1470 and 1598 cm^{-1} in the tunneling spectrum:² shifts

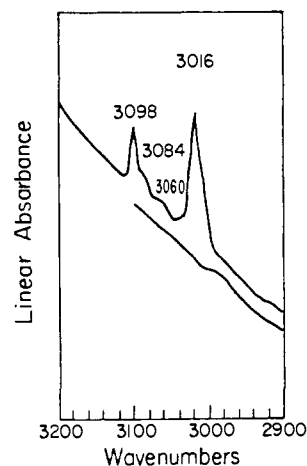
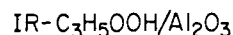


Figure 2. Infrared spectrum of Al_2O_3 powder exposed to 1500 torr-cyclopropanecarboxylic acid vapor.

of $+57$ and $+42\text{ cm}^{-1}$, respectively. Therefore, by analogy to the surface acetate species,² the bonding of cyclopropanecarboxylate to the surface is evidently bidentate, symmetrical bridging through the carboxylate moiety.

3.4. $\nu(\text{CH}_2)$ and $\nu(\text{CH})$ Modes above 3000 cm^{-1} . The C–H stretching modes of the sodium salt of cyclopropanecarboxylic acid all lie above 3000 cm^{-1} . Hence, it is convenient to consider first those bands in the tunneling spectrum above 3000 cm^{-1} , which, in direct analogy to the sodium salt, are due to a cyclopropanecarboxylate adspecies.

The free anion has five CH stretching modes (cf. Table I). These are the A' and A'' $\nu_s(\text{CH}_2)$, the A' and A'' $\nu_a(\text{CH}_2)$, and the A' $\nu(\text{CH})$ modes. However, the Raman spectrum of the free anion shows only four peaks, the two lowest lying CH stretching modes [A' $\nu(\text{CH})$ and A'' $\nu_s(\text{CH}_2)$] being unresolved.

The two highest lying modes (the two CH_2 asymmetric stretching modes) are only split by 12 cm^{-1} in the Raman spectrum. Since the instrumental broadening function of the tunneling spectrometer is approximately 14 cm^{-1} in the best scans of this spectral region, two Lorentzian functions would be unresolved. Hence, the tunneling peak at 3084 cm^{-1} (fwhm = 50 cm^{-1}) is assigned to this combination of modes (cf. Table I). Comparing the tunneling peak at 3084 cm^{-1} to the Raman center of mass for these two asymmetric stretching modes (of nearly equal Raman intensity), a shift of approximately -5 cm^{-1} is found. This is in good agreement, for example, with the results of Evans and Weinberg who found shifts ranging from -6 to -15 cm^{-1} between tunneling and optical spectra of CH stretching modes in ethanol chemisorbed on Al_2O_3 .²

The two lowest lying CH stretching modes of the free anion are the A'' $\nu_s(\text{CH}_2)$ mode and the composite of the A' $\nu_s(\text{CH}_2)$ and A' $\nu(\text{CH})$ modes, occurring at 3048 and 3018 cm^{-1} , respectively, in the Raman spectrum. However, the corresponding region in the tunneling spectra shows only one peak at 3001 cm^{-1} (fwhm = 50 cm^{-1}). This would reasonably correspond to the lowest frequency CH stretching mode of the free anion. For the free anion, the Raman bands for these two modes are split by approximately 30 cm^{-1} , and this should be resolvable in the tunneling spectrum. The conspicuous absence of the A'' $\nu_s(\text{CH}_2)$ mode requires further investigation. Consequently, IR measurements with $\text{C}_3\text{H}_5\text{COOH}$ adsorbed on Al_2O_3 were carried out in order to confirm the tunneling spectroscopic findings. As may be seen in Figure 2, four $\nu(\text{CH}_2)$ modes were visible, corresponding closely (within $\pm 2\text{ cm}^{-1}$) to the Raman spectrum of the sodium salt. The A' $\nu_s(\text{CH}_2)$ mode, the strongest IR mode, has a full width at half-maximum of approximately 20 cm^{-1} . The A'' $\nu_s(\text{CH}_2)$ and A' $\nu_a(\text{CH}_2)$ modes were observed as a less intense peak (fwhm

(28) A. J. Maeland, R. Rittenhouse, W. Lahar, and P. V. Romano, *Thin Solid Films*, **21**, 67 (1974).

(29) K. Ito and H. J. Bernstein, *Can. J. Chem.*, **34**, 170 (1956).

$\approx 16 \text{ cm}^{-1}$) with a small shoulder. Curiously, the $A'' \nu_s(\text{CH}_2)$ mode was barely visible. Hence, the "absence" of the corresponding mode in the tunneling spectrum is probably due to its being only a weakly active mode that is buried between the remaining two intense C-H stretching modes.

The broad line width ($>40 \text{ cm}^{-1}$) of the two $\nu(\text{CH}_2)$ modes in the tunneling spectrum may be explained by realizing that two modes are responsible for the intensity of each peak. Different downshifts in frequency due to image-dipole interactions for each mode increase the frequency splitting, broadening the peaks.³⁰ The distance between the CH_2 groups and the lead overlayer may vary from molecule to molecule, giving a distribution of frequency shifts. The shape of the ring breathing mode supports this idea. It is the narrowest spectral line and, since its dipole derivative is most remote from the lead overlayer (without suffering lifetime broadening), it experiences only weak image-dipole shifts.

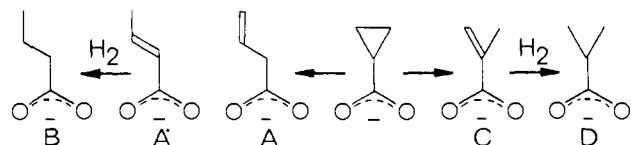
3.5. $\nu(\text{CH}_2)$ Modes below 3000 cm^{-1} . There are clearly no vibrational modes of the adsorbed cyclopropanecarboxylate anion that would reasonably yield the observed low-frequency peaks at $2970\text{--}2840 \text{ cm}^{-1}$ in Figure 1f. Therefore, to explain the existence of these peaks, it is necessary to postulate the existence of another surface species in addition to the cyclopropanecarboxylate anion.

4. *n*-Butyrate Surface Species

For the majority of carboxylic acids studied (e.g., saturated hydrocarbons), at room temperature the Al_2O_3 surface exhibits little affinity or reactivity for the hydrocarbon group, as evidenced by little or no perturbation in the CH stretching vibrations. This is true also for cyclopropanecarboxylic acid in the sense that (as we have identified in Figure 1f) there are CH stretching modes present in the tunneling spectrum that correspond closely to the CH stretching frequencies of the sodium salt of this acid. However, there is also a moderately strong CH stretching band in the tunneling spectrum that is not present in the IR or Raman spectra of the sodium salt. Furthermore, this CH stretching band is present (with undiminished intensity) in the other tunneling spectra of Figure 1, as well as in Figure 3c where $\text{C}_3\text{H}_5\text{COOH}$ is exposed to an alumina surface heated to 550 K. In the latter, the intensity of this CH stretching band has increased markedly.

The appearance of the strong carbon-hydrogen stretching bands at 2962, 2908, and a shoulder at $2860\text{--}2870 \text{ cm}^{-1}$ with intensity comparable to the $\nu(\text{CH}_2)$ modes of the adsorbed cyclopropanecarboxylate anion is certain evidence for the existence of a second adsorbed hydrocarbon species (cf. Figure 3c). The spectral regions where the $\delta_s(\text{CH}_2)$ and $\nu_s(\text{COO}^-)$ modes of adsorbed $\text{C}_3\text{H}_5\text{COO}^-$ appear also show new vibrational modes. It is clear that the surface species responsible for these additional modes is a carboxylate anion since modes corresponding both to $\nu_a(\text{COO}^-)$ and $\tau(\text{C-COO}^-)$ remain strong despite a significant reduction in the $\text{C}_3\text{H}_5\text{COO}^-$ surface population.

Bearing in mind that the chemical transformation undergone by the $\text{C}_3\text{H}_5\text{COO}^-$ is undoubtedly some form of ring opening, a list of likely reaction products is readily enumerable:



In Figure 3c, the absence of carbon-carbon multiple bond stretching modes, coupled with the paraffinic character of the unidentified carbon-hydrogen stretching modes, is compelling evidence that the second surface species is a paraffinic hydrocarbon. In fact, the tunneling spectrum of adspecies A', crotonate, has been reported¹ and shows a carbon-carbon double bond stretching mode as well as other modes that are absent in our spectra. These arguments eliminate the unsaturated species (A, A', and C) indicated above, in favor of one or both of the saturated species (B and/or D). Vibrational modes attributable to the $\nu_a(\text{CH}_3)$ (2940 cm^{-1}), the $\nu_s(\text{CH}_3)$ ($2880\text{--}2860 \text{ cm}^{-1}$, sh) and the

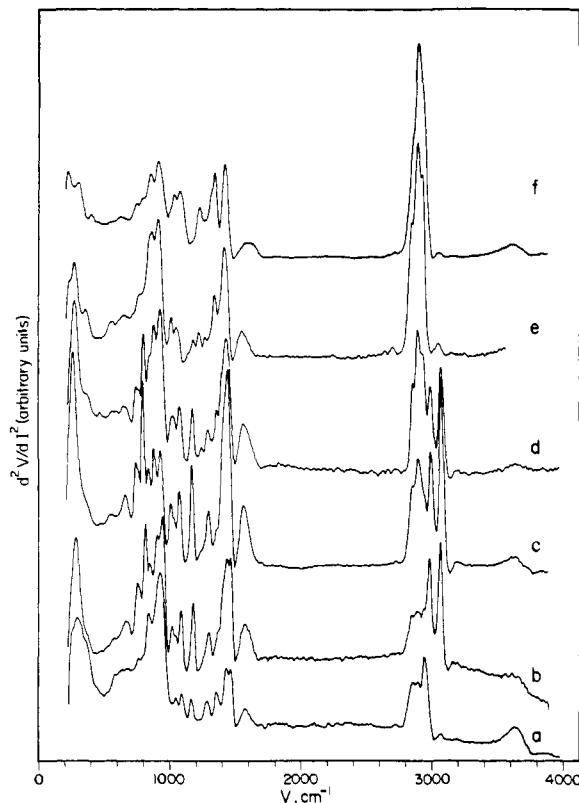


Figure 3. Inelastic electron tunneling spectra of (a) Al_2O_3 at 295 K exposed to 0.21 torr-s isobutyric acid; (b) Al_2O_3 at 295 K to 0.09 torr-s cyclopropanecarboxylic acid followed by exposure to 0.18 torr-s isobutyric acid; (c) Al_2O_3 heated to 550 K while exposed to 0.4 torr-s of cyclopropanecarboxylic acid; (d) Al_2O_3 at 295 K exposed to 0.09 torr-s cyclopropanecarboxylic acid followed by exposure to 0.18 torr-s *n*-butyric acid; (e) Al_2O_3 at 295 K exposed to 0.18 torr-s *n*-butyric acid; and (f) Al_2O_3 at 295 K exposed to a 0.0016 M solution of 2-hydroxy-*n*-butyric acid in H_2O .

$\delta_s(\text{CH}_3)$ (1380 cm^{-1}) identify a methyl group, while modes attributable to the $\nu_a(\text{CH}_2)$ (2908 cm^{-1}) and the $\nu_s(\text{CH}_2)$ ($2870\text{--}2860 \text{ cm}^{-1}$, sh) indicate the presence of a methylene group.³¹ Other strong stretching modes characteristic of these groups [$\delta_a(\text{CH}_3)$ ($1480\text{--}1430 \text{ cm}^{-1}$) and $\delta_s(\text{CH}_2)$ ($1490\text{--}1450 \text{ cm}^{-1}$)³¹ most certainly occur, but they are unresolved in the broad loss (fwhm $\approx 80 \text{ cm}^{-1}$) at 1450 cm^{-1} that also contains another mode for this species [$\nu_s(\text{COO}^-)$], in addition to modes from the unreacted $\text{C}_3\text{H}_5\text{COO}^-$ [$\nu_s(\text{COO}^-)$ and $\delta(\text{CH}_2)$]. These observations argue in favor of *n*-butyrate (species B) as the product of reaction. However, the existence of the isobutyrate species (D) cannot be ruled out completely. Because of the rather broad line widths intrinsic to tunneling spectroscopy, it is impossible to isolate modes, such as skeletal vibrations, unique to species B or D and yet free from interfering bands of other surface species. Nevertheless, it has been possible to reduce the number of candidate surface species to either *n*-butyrate (B) and/or isobutyrate (D).

To provide positive identification, isobutyric acid and *n*-butyric acid were adsorbed independently on Al_2O_3 . The resulting tunneling spectra for alumina exposed to 0.21 torr-s of isobutyric acid at 295 K, and for alumina exposed to 0.18 torr-s of *n*-butyric acid at 295 K are shown in Figures 3a and 3e, respectively.³² To reproduce closely the expected distribution of surface species from $\text{C}_3\text{H}_5\text{COOH}$ adsorbed on alumina heated above 500 K (Figure 3c), *n*-butyric acid and cyclopropanecarboxylic acid were coad-

(31) D. Dolphin and A. Wick, "Dolphin Tabulation of Infrared Spectral Data", Wiley, New York, 1977; L. J. Belamy, "The Infrared Spectra of Complex Molecules", Wiley, New York, 1956; L. M. Sverdlov, M. A. Kovner, and E. P. Krainov, "Vibrational Spectra of Polyatomic Molecules", Wiley, New York, 1974.

(32) Brown et al. (see ref 5) have published the spectrum of $\text{C}_3\text{H}_7\text{COOH}/\text{Al}_2\text{O}_3$, and peak positions and intensities reported there correspond very well with our work.

(30) J. R. Kirtley and P. K. Hansma, *Phys. Rev. B*, **12**, 531 (1975).

sorbed on alumina at 295 K (Figure 3d). Isobutyric acid and cyclopropanecarboxylic acid were also coadsorbed on alumina at 295 K (Figure 3b) to check for the other possible combination of surface species (i.e., isobutyrate and cyclopropanecarboxylate). A comparison of the tunneling spectrum of alumina exposed to 0.4 torr-s of C_3H_5COOH at 550 K (Figure 3c) and the tunneling spectrum of alumina exposed to $n-C_3H_7COOH$ and C_3H_5COOH at 295 K (Figure 3d) gives an exceedingly close match, except for intensity differences due to the imperfect match in the relative populations of $n-C_3H_7COO^-$ and $C_3H_5COO^-$ on each surface. On the other hand, a comparison of the tunneling spectrum of alumina exposed to 0.4 torr-s C_3H_5COOH at 550 K (Figure 3c) and the tunneling spectrum of alumina exposed to $i-C_3H_7COOH$ and C_3H_5COOH at 295 K (Figure 3b) is an obvious mismatch. The twin peak structure of the combination of the $\delta(CH_2)$, $\delta_a(CH_3)$, $\delta_s(CH_3)$, and $\nu_s(COO^-)$ modes apparent in Figure 3b is absent from Figure 3c, nor is the structure of the CH stretching region in Figure 3b reproduced in Figure 3c. Thus, within the detectability limit, isobutyrate is not present on the surface. It can be concluded that cyclopropanecarboxylic acid chemisorbs on plasma-grown alumina as either the cyclopropanecarboxylate anion or the n -butyrate anion, depending upon the surface temperature and surface coverage.

Surface hydroxyls on TiO_2 reportedly add across the carbon-carbon double bond of cyclohexene to form a surface cyclohexanolate.³³ Homogeneous analogues of this reaction, such as the acid-catalyzed hydration of a carbon-carbon double bond, have been studied extensively.³⁴ These reactions suggest that acidic or electrophilic surface hydroxyls must be responsible for the observed hydrations on TiO_2 . Although measurements indicate the surface acidity of Al_2O_3 is substantially less than TiO_2 ,³⁵ in light of the unprecedented observation of hydrogenolysis that is reported here, it is important to verify that we are not in fact observing a hydration reaction. This is especially true in view of the expected close similarity in spectra between the n -butyrate and the possible hydration product of cyclopropanecarboxylate, namely, 2-hydroxy- n -butyrate. This latter isomer is expected to be the preferred product based on the acid-catalyzed isomerization of methylcyclopropane over $SiO_2-Al_2O_3$ where the acid proton attacks one of the vinyl carbons.¹³ Therefore, an aluminum oxide surface was exposed to a 0.0016 M solution of 2-hydroxy- n -butyric acid in H_2O . The resulting tunneling spectrum is shown in Figure 3f. The C-H stretching region in this spectrum (Figure 3f) compares unfavorably with the aliphatic C-H stretching region in the spectrum of cyclopropanecarboxylic acid adsorbed at 550 K (Figure 3c); for example, in the former spectrum, the C-H stretching region does not show the distinct shoulder at 2860 cm^{-1} that is visible in the latter spectrum. Consequently, the products of a hydration reaction are not present on the surface of Al_2O_3 exposed to C_3H_5COOH above 550 K, and this strengthens further our earlier identification of n -butyrate as the only reaction product.

5. Surface Hydrogenolysis Reaction

5.1. Isotopic Studies. To gain further insight into the reaction mechanism whereby the adsorbed cyclopropanecarboxylate is converted to the n -butyrate, isotopic labeling experiments were performed. These experiments consisted of producing a plasma-grown alumina surface that had surface deuterioxy groups rather than surface hydroxyl groups. The deuterium-labeled alumina surface was then exposed to 0.036 torr-s of deuterium-labeled cyclopropanecarboxylic acid (C_3H_5COOD) at 295 K. This surface was then heated to 573 K under vacuum. Tunneling spectra from junctions completed after each of these three steps are shown, respectively, in Figures 4a-c. These spectra are similar to the analogous spectra of the unlabeled surface exposed to the

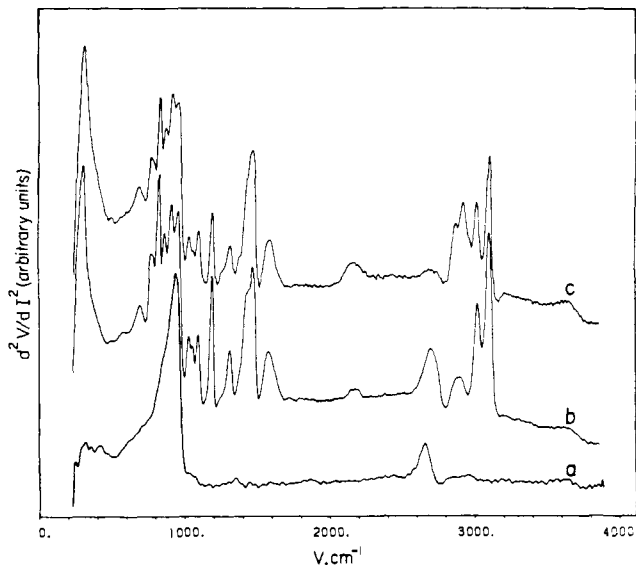


Figure 4. Inelastic electron tunneling spectra of a deuterated alumina surface exposed to cyclopropanecarboxylic acid: (a) tunneling spectrum of clean Al_2O_3 junction showing nearly complete exchange of surface OH groups with OD groups; (b) as in (a) except the surface was exposed to 0.038 torr-s cyclopropanecarboxylic acid- $O-d$ at 295 K; and (c) as in (b) except the surface was subsequently heated in vacuo to 573 K.

unlabeled acid with the exception of two features. These are the OD stretching mode at 2668 cm^{-1} (Figure 4a) rather than the OH stretching mode at 3600 cm^{-1} (for clean plasma-grown alumina surfaces), and the broad ($\sim 120\text{-cm}^{-1}$ fwhm) carbon-deuterium stretching mode centered at 2172 cm^{-1} . Comparing the tunneling spectrum of C_3H_5COOD adsorbed on the surface before heating (Figure 4b) to the tunneling spectrum of C_3H_5COOD adsorbed on the surface after heating to 573 K (Figure 4c), it is apparent that several significant changes have taken place. The intensity of the OD stretching mode at 2668 cm^{-1} has decreased, and, concomitantly, the intensity of the CD stretching mode has increased. Clearly, deuterium has been transferred from OD groups to form carbon-deuterium bonds. The carbon-deuterium modes are almost certainly not the result of exchange between the deuterioxy and the hydrogen in the adsorbed cyclopropanecarboxylate species. If this were the case, the OH stretching mode would show an increase in intensity comparable to the decrease in intensity of the OD stretching mode (assuming reasonably equivalent cross sections for deuterium and hydrogen). However, within experimental error, the intensity of the OH mode remains unchanged. Hence, it can be concluded that the hydrogenolysis of cyclopropanecarboxylate adsorbed on Al_2O_3 involves the transfer of hydrogen from the surface hydroxyls to form additional carbon-hydrogen bonds. If the integrated intensity of the C-D stretching mode is compared with the integrated intensity of the aliphatic C-H stretching mode, a ratio of 2.2 to 5.0 is found. This is very close to the expected ratio of 2:5 if it is assumed that C-D and C-H vibrations have identical cross sections. This confirms that hydrogen from two surface hydroxyls is transferred to the cyclopropanecarboxylate to form the n -butyrate species.

The final point of interest concerning the carbon-deuterium stretching mode is its fwhm of $\sim 120\text{ cm}^{-1}$. This is approximately the same as the fwhm of the combined aliphatic C-H stretching modes. Infrared studies have shown the carbon-deuterium stretching frequency to shift from 2169 to 2154 cm^{-1} as the deuterium location shifts from the methyl group in 1-deuteriopropane to the methylene group in 2-deuteriopropane. This indicates that as the adsorbed cyclopropanecarboxylate undergoes hydrogenolysis to form the n -butyrate adspecies, the deuterium that is effecting hydrogenolysis is incorporated onto *different* carbon centers in the hydrogenolysis product.

5.2. Coverage- and Temperature-Dependent Reactivity of the Al_2O_3 Surface. At a constant temperature of 295 K, the coverage

(33) H. P. Boem and H. Knözinger in "Catalysis Science and Technology", Vol. 4, J. R. Anderson and M. Boudart, Eds., Springer-Verlag, New York, 1983, p 177.

(34) T. H. Lowry and K. Richardson, "Mechanism and Theory in Organic Chemistry", Harper and Row, New York, 1976.

(35) K. Tanabe in "Catalysis Science and Technology", Vol. 2, J. R. Anderson and M. Boudart, Eds., Springer-Verlag, New York, 1981, p 231.

dependence of the populations of the *n*-butyrate and cyclopropanecarboxylate adspecies yields information concerning the coverage-dependent reactivity of the Al_2O_3 surface (cf. Figure 1). The stretching modes associated with the *n*-butyrate ($2935\text{--}2830\text{ cm}^{-1}$) are the first CH modes to appear after low exposures of the Al_2O_3 surface to $\text{C}_3\text{H}_5\text{COOH}$ (cf. Figure 1b). With increasing exposure, these modes cease to increase in intensity (or increase little), while the CH modes of the cyclopropanecarboxylate ($3001\text{--}3081\text{ cm}^{-1}$) continue to increase dramatically in intensity (cf. Figures 1c–f). This implies that cyclopropanecarboxylate undergoes hydrogenolysis on the alumina surface at low coverages, even at 295 K. As the surface coverage increases, the differential concentration of adsorbed cyclopropanecarboxylic acid is significantly less likely to undergo hydrogenolysis. An estimate of the number of reacted molecules on the Al_2O_3 surface at 295 K can be made by calculating the relative areas of the CH modes below 3000 cm^{-1} compared to those above 3000 cm^{-1} . This assumes that the electron-vibrational coupling constant of CH modes is independent both of symmetry and chemical species. On this basis, one concludes that approximately 25% of the chemisorbed molecules undergo hydrogenolysis at 295 K.

At a fixed exposure of 0.4 torr-s, the temperature dependence of the population of the hydrogenated species gives information concerning its formation. As judged by the spectral band between 2800 and 2980 cm^{-1} , the surface population of the *n*-butyrate remains small and nearly constant, independent of temperature, until approximately 460 K. (Although not shown here, tunneling spectra of alumina exposed to $\text{C}_3\text{H}_5\text{COOH}$ at temperatures below 450 K are virtually identical with their unheated counterparts shown in Figure 1.) Between 460 and 500 K, the population of *n*-butyrate increases as shown in Figure 3c. However, a further increase in the surface temperature results in little increase in the concentration of the cyclopropanecarboxylate hydrogenolysis product. The motion of protons on Al_2O_3 has been explored by NMR only at temperatures below 400 K.³⁶ Consequently, calculations of the rate of thermal diffusion of protons cannot be made for this surface, since thermal spin diffusion is not the dominant mechanism of relaxation over this temperature regime. However, studies of protons on decationized zeolites indicate that the proton diffusion coefficient, expressed in terms of a jump frequency, increases from 0.2 s^{-1} at 300 K to $2.2 \times 10^4\text{ s}^{-1}$ at 473 K, to $1.5 \times 10^5\text{ s}^{-1}$ at 525 K, where the jump distance is approximately 4.4 \AA .³⁷ Presumably, the significantly enhanced rate of proton diffusion at high temperatures is largely responsible for the observed rapid increase in the population of the *n*-butyrate.

Diffusion, however, is an activated process, and if solely responsible for surface hydrogenation, the surface population of hydrogenated species would show an exponential temperature dependence. This is not the case, however. Rather, above 500 K at constant coverage, the ratio of hydrogenated to unreacted surface populations remains remarkably invariant, increasing only slightly between 500 and 700 K. Certainly the reaction is not hydrogen limited: a moderate hydroxyl stretching mode attests to the availability of surface hydrogen (cf. Figure 4c). On the other hand, possible hydroxyl sites around an adsorbate molecule could be statistically blocked on a nearly saturated surface. Since the carboxylate is immobile, this would effectively limit the $\text{C}_3\text{H}_5\text{COO}^-$ available for reaction.

5.3. Mechanism of the Hydrogenolysis Reaction. Tunneling spectroscopy has been used previously to investigate the hydrogenation of carbon-carbon double and triple bonds on alumina. Brown et al.⁴ observed a mixture of hydrogenated products and parent molecules on Al_2O_3 barriers of tunnel junctions exposed to $\text{HC}\equiv\text{CCOOH}$, $\text{H}_2\text{C}=\text{CHCOOH}$, and 3-methylbut-2-enoic acid at room temperature. McBride and Hall⁹ investigated the temperature-dependent incorporation of deuterium from D_2O

vapor into muconic acid ($\text{HCOOC}-\text{HC}=\text{CH}-\text{HC}=\text{CH}-\text{COOH}$) adsorbed on Al_2O_3 barriers of tunnel junctions. The deuterium was incorporated by deuteration of the double bonds to form adipate, the corresponding saturated hydrocarbon. Jaklevic¹⁰ has examined the hydrogenation and deuteration of $\text{HC}\equiv\text{CCOOH}$ in tunnel junctions exposed to this acid at room temperature. In all cases, the source of hydrogen was concluded to be surface hydroxyl groups. The present work, however, is the first observation of ring hydrogenolysis where carbon-carbon bonds are broken, and the hydrocarbon skeletal structure is changed.

Since isomerization is intrinsically faster than hydrogenation, and since identical sites on dehydroxylated Al_2O_3 powders catalyze both isomerization (1-butene) and hydrogenation (ethylene),¹⁵ it may be correct to view the hydrogenolysis as an isomerization followed by a hydrogenation. Then, the observed selectivity of the hydrogenolysis of cyclopropanecarboxylate to *n*-butyrate may be a consequence of the selectivity of Al_2O_3 powders to isomerize methylcyclopropane to *trans*-2-butene.³⁸ Certainly this is not a completely fortuitous result since thermal isomerization of methylcyclopropane yields a uniform distribution of isomers,¹⁴ and hydrogenolysis of methylcyclopropane by platinum on an inactive silica support yields isobutanes.¹⁹ Although the isomerization of methylcyclopropane over $\text{SiO}_2\text{-Al}_2\text{O}_3$ also yields strictly *n*-butenes,¹³ the isomerization mechanism over these catalysts involves proton transfer *from the surface* to the hydrocarbon to form the carbocation,¹³ whereas the isomerization mechanism over Al_2O_3 involves proton transfer *to the surface* to form the carbanion.^{11,12} Although the hydrogenolysis product is in accord with dehydroxylated Al_2O_3 powders, there are a number of important distinctions between these catalytically active materials and the aluminum oxide film. In particular, on Al_2O_3 powders the active sites, which are thought to be created by dehydroxylation at very high temperatures, have an extremely low density, which is estimated to be on the order of 1.4×10^{13} sites cm^{-2} for hydrogenation below 333 K and as low as 1.6×10^{12} sites cm^{-2} for hydrogenation above 333 K.¹⁵ In contrast, these numbers are to be compared with the concentration of active sites for hydrogenolysis on the aluminum oxide films which were not produced by high-temperature pretreatment (via the number of adsorbed cyclopropanecarboxylates that underwent hydrogenolysis in Figure 3c), namely $1.1 \times 10^{14}\text{ cm}^{-2}$. Several very reasonable assumptions were made to arrive at this figure: (1) the (100) surface plane of $\gamma\text{-Al}_2\text{O}_3$ is preferentially exposed;³⁹ (2) adsorption sites consist of pairs of octahedrally coordinated aluminum ions of the (100) surface; (3) the surface in Figure 3c is saturated; and (4) the relative coverage of the cyclopropanecarboxylate to the *n*-butyrate is 2:1. Furthermore, on the Al_2O_3 powder, the experimental evidence supports a hydrogenation mechanism involving adsorbed ethylene and molecularly adsorbed H_2 ,¹⁵ whereas on the aluminum oxide films, the surface hydroxyls provide hydrogen and there is no source of gaseous hydrogen. Thus, the hydrogenation mechanisms for Al_2O_3 powders would not fully explain the hydrogenation and hydrogenolysis results observed on aluminum oxide films.

However, a boehmite/ $\gamma\text{-Al}_2\text{O}_3$ prepared from Al_2O_3 powder exhibits behavior that is remarkably similar to what has been reported here.¹⁶ For example, the concentration of active sites was measured (by HCl poisoning) to be between 1×10^{14} and 0.4×10^{14} sites cm^{-2} for different preparations. Furthermore, high-temperature activation was unnecessary, and, in fact, the deactivated material was regenerated with steam. The surface was active for both isomerization and hydrogenation of 1-pentene and 1,3-butadiene. Although the material was referred to as a "catalyst", it exhibited a stoichiometric behavior. In most instances, during the hydrogenation of 1-pentene, the activity of the material decreased slowly with time. Furthermore, the turnover number (number of 1-pentene molecules hydrogenated per site per hour) calculated for the most active material was 0.2. Thus to substantiate "catalytic" activity, the catalysts must

(36) B. Stubner, H. Knözinger, J. Conard, and J. J. Friplatt, *J. Phys. Chem.*, **82**, 1811 (1978).

(37) W. N. Delegass, G. L. Haller, R. Kellerman, and J. H. Lunsford in "Spectroscopy in Heterogeneous Catalysis", Academic Press, New York, 1979.

(38) Y. Amenomiya, *J. Catal.*, **46**, 326 (1977).

(39) H. Knözinger and P. Ratnasamy, *Catal. Rev. Sci. Eng.*, **17**, 31 (1976).

necessarily be run for at least 5 h, whereas typical run times were no longer than 1 h.

However, there is no spectroscopic evidence for the presence of bohemite on our aluminum oxide films. In the concentrations necessary for the observed behavior, the bohemite would be detectable easily by the presence of a mode at 1070 cm^{-1} , as reported in the IR spectrum of bohemite powders,⁴⁰ whereas the clean aluminum oxide film does not have a mode in this vicinity.

Although metal oxides such as ZnO and MgO are active for hydrogenation/dehydrogenation, the active site on these materials is thought to involve a metal hydride. Though there is evidence for Al-H at the Al/Al₂O₃ interface of Al/Al₂O₃Pb tunnel junctions,⁴¹ because of the rapid gettering action of low-valent aluminum with residual H₂O, this type of structure is not likely to be present at the Al₂O₃/vacuum interface.

6. Synopsis

The temperature- and coverage-dependent interaction of cyclopropanecarboxylic acid with aluminum oxide has been studied with tunneling spectroscopy. The coverage-dependent work was carried out at room temperature, while the temperature-dependent work was conducted at constant coverage with the temperature varied between 295 and 700 K. The Al₂O₃ surface was synthesized by plasma oxidation of aluminum films. Two species were formed upon adsorption, the relative populations of which were a function of coverage and temperature. A comparison of the IR and Raman spectra of sodium cyclopropanecarboxylate and the tunneling spectra of the acid adsorbed on Al₂O₃ indicates that one of the two surface species is cyclopropanecarboxylate coordinated to the surface through the carboxylate group as a symmetrical bidentate

ion. The population of the cyclopropanecarboxylate species was dominant at high coverages on Al₂O₃ surfaces held at room temperature. At low coverages and room temperature, the second surface species, an *n*-butyrate, was dominant. If the Al₂O₃ surface was exposed to cyclopropanecarboxylic acid at room temperature and subsequently heated above 500 K, the intensity of the carbon-hydrogen stretching modes due to the *n*-butyrate increased at least threefold. Coadsorption of *n*-butyric acid and cyclopropanecarboxylic acid on the Al₂O₃ surface at room temperature resulted in spectra that closely matched the tunneling spectra of cyclopropanecarboxylic acid adsorbed on Al₂O₃ at temperatures above 500 K, verifying the identification of *n*-butyrate coordinated to the surface through the carboxylate group. Isotopic labeling of the surface hydroxyls with deuterium, followed by adsorption of the cyclopropanecarboxylic acid, resulted in a surface species with carbon-deuterium stretching vibrations. Thus, the *n*-butyrate must be the product of a hydrogenolysis reaction in which the hydrogen atoms are supplied by hydroxyl groups present on the Al₂O₃ surface. No stable intermediates were found prior to the formation of the *n*-butyrate surface species. Coadsorption of cyclopropanecarboxylic acid and isobutyric acid on Al₂O₃ at room temperature resulted in spectra that correlated poorly with the spectra of cyclopropanecarboxylic acid adsorbed on Al₂O₃ at temperatures above 500 K. Consequently, the other possible species resulting from ring opening and hydrogenation, isobutyrate, is not formed.

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Registry No. Al₂O₃, 1344-28-1; C₃H₅COOH, 1759-53-1; CH₃CH₂C-
H₂COOH, 107-92-6; butyrate, 461-55-2.

(40) L. D. Frederickson, *Anal. Chem.*, **12**, 1883 (1954).
(41) S. Gauthier, S. De Cherveigne, J. Klein, and M. Belin, *Phys. Rev. B*, submitted for publication.

Estimation of the Rate of Electron Transfers between Two Contacting Polymer Surfaces

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Abstract: A bilayer of redox polymer films, Pt/poly[Os(bpy)₂(vpy)₂]²⁺/poly[Ru(vbpy)₃]²⁺, is coated on a Pt electrode. Reduction of the poly[Ru]³⁺ outer film of a preoxidized bilayer, Pt/poly[Os]³⁺/poly[Ru]³⁺, is controlled by the rate of electron diffusion through the inner, poly[Os]^{2+/3+} film. When oxidizing the outer poly[Ru]²⁺ film of a reduced Pt/poly[Os]²⁺/poly[Ru]²⁺ bilayer, however, the rate of oxidation depends largely on the kinetics of electron transfer between the ca. monolayer of poly[Os]³⁺ and poly[Ru]²⁺ sites in contact at the interface between the two polymer films. The electron diffusion kinetics in the two polymer films perturb the interfacial reaction rate only slightly, so that a lower limit to the interfacial electron transfer rate constant is available. Remarkably, this value is within a factor of ca. 28 of that calculated from the Marcus relation for the corresponding homogeneous cross-reaction-transfer reaction in acetonitrile.

Ultrathin (10–1000 nm), stable, and adherent films of the electroactive transition-metal polymers poly[M(bpy)₂(vpy)₂]²⁺ and poly[Ru(vbpy)₃]²⁺, where M = Os or Ru, vbpy = 4-vinyl-4'-methyl-2,2'-bipyridine, and vpy = 4-vinylpyridine, are easily electropolymerized onto Pt electrodes from monomer complex solutions.^{1,2} These films and those of analogous complexes have provided a number of important insights into the internal electron self-exchange,^{3,4} permeation,⁵⁻⁷ and electron-transfer-mediation chemistry⁶⁻⁹ of transition-metal polymers. This paper further

exploits this electron-transfer chemistry to arrive at an estimate of the rate of an electron-transfer reaction between two different,

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