



Princeton University Library
Document Delivery Service
Firestone Library A-8-E
docdel@princeton.edu
609-258-7469

Thank you for using Princeton University Library's Document Delivery Service. We are happy to meet your research needs.

Please note that we can only host your electronic article for **21 days** from the date of delivery. After that, it will be **permanently deleted**.

As always, feel free to contact us with any questions or concerns.

WARNING CONCERNING COPYRIGHT RESTRICTIONS

The copyright law of the United States (Title 17, United States Code) governs the making of photocopies or other reproductions of copyrighted materials.

Under certain conditions specified in the law, libraries and archives are authorized to furnish a photocopy or other reproduction. One of these specified conditions is that the photocopy or reproduction is not to be "used for any purpose other than private study, scholarship, or research". If a user makes a request for, or later uses, a photocopy or reproduction for purposes in excess of "fair use", that user may be liable for copyright infringement.

This institution reserves the right to refuse to accept a copying order if, in its judgment, fulfillment of the order would involve violation of copyright law.



Please consider the environment before printing

EDD RETRIEVAL RECEIPT

Order: 477331
For: EDD
Copied: 01/10/2018
Shipped: 01/10/2018
Deliver To: 22101002534147
Patron E-Mail: docdel@princeton.edu
Oth Patron Info:
Def PickUp Loc: EDD-ReCAP EDD
Delivery Meth: EDD

Item BarCode: 32101061096127
Item Title: Journal of vacuum science & technology. an official journal
Item Author:
Item Call Number: TJ940 .J668
Item Vol/Part:

Article Title: THE FORMATION OF ACETIC-ANHYDRIDE BY DECOMPOSITION
Article Author: ERLEY, W
Art Vol/Part: 2nd ser., v. 8,
Beg Page: 976 End Page: 978 Total Pages: 0
Other Info:
Notes: TN936762, save to images folder for AE (QA)

The formation of acetic anhydride by decomposition of acetic acid adsorbed on Ni(111)

W. Erley, J. G. Chen, and D. Sander

*Institut für Grenzflächenforschung und Vakuumphysik der Kernforschungsanlage Jülich GmbH,
D-5170 Jülich, Federal Republic of Germany*

(Received 12 September 1989; accepted 18 November 1989)

Recently,¹ thermal desorption spectroscopy (TDS) and reflection-absorption infrared spectroscopy (RAIRS) were used to characterize the stable surface intermediate that forms after the decomposition of formic acid adsorbed on a clean Ni(111) surface. Whereas on other single-crystal surfaces, a formate ion (HCOO^-) has been postulated as a likely surface reaction intermediate, we found strong evidence from an isotopic mixing experiment that the reaction intermediate formed on Ni(111) by the decomposition of formic acid (HCOOH) is formic anhydride (HCO_2O). Unfortunately, a direct comparison between the infrared (IR) spectrum of the surface reaction intermediate and that of adsorbed formic anhydride is not possible because the latter is not a stable compound.

The purpose of the present work is to examine the adsorption and thermal decomposition of acetic acid (CH_3COOH) adsorbed on Ni(111), as unlike formic anhydride, acetic anhydride is a stable compound and hence, its IR spectrum is directly comparable to the IR spectrum of the intermediate, which is formed on the Ni(111) surface by decomposition of acetic acid after heating to 250 K. Our results clearly indicate that the reaction intermediate obtained after the decomposition of acetic acid is acetic anhydride.

The adsorption and decomposition of acetic acid has been studied on several single crystal surfaces using various surface sensitive techniques: high resolution electron energy loss spectroscopy (EELS) has been applied in the case of acetic acid adsorbed on the surfaces of Cu(100),^{2,3} Pt(111),⁴ and Al(111).⁵ In all cases, the formation of a surface acetate species (CH_3COO^-) was suggested, after heating the acetic acid covered samples to 250 K. Photon electron spectroscopy (XPS, UPS) and TDS have been employed to study the adsorption and decomposition of acetic acid on a Cu(110)⁶ surface. Both acetate and acetic anhydride have been postulated as possible surface intermediates after the thermal decomposition of acetic acid. On Ni(111),⁷ thermal desorption spectra of acetic acid and acetic anhydride, taken after adsorption at 250 K, have been compared directly to each other. Slight differences in the spectra led to the conclusion that the intermediate that is formed by decomposition of acetic acid on the Ni(111) surface is not identical to adsorbed acetic anhydride. In consequence, the intermediate species was assigned to an acetate ion. However, it should be noted here, that similar to the formic acid/Ni(111) system, dehydration of acetic acid adsorbed on Ni(110) at temperatures below 250 K has been reported in a study by Madix *et al.*⁸

Because of the high instrumental resolution of the RAIRS, this technique was used in the present study to char-

acterize the intermediate, which is formed by the dehydration of adsorbed acetic acid, as well as adsorbed acetic anhydride. In addition, we reinvestigated the desorption behavior of both acetic acid and acetic anhydride in order to reproduce the TDS results of Schoofs and Benziger⁷ and to obtain additional information to identify the surface reaction intermediate. The dosing of the acetic acid was always done under conditions where the concentration of dimers was much higher than the monomer concentration.

The mass spectrometer was used in a multiplexed mode so that up to 10 masses could be monitored simultaneously. The heating rate was 1 K/s. Figures 1(a)–1(e) shows the evolution of the masses, 2, 28, 44, 18, and 15 from the decomposition of acetic acid (left panel) as well as of acetic anhydride (right panel) after the adsorption on Ni(111) at 85 K. The predominant observation is that the two compounds show identical decomposition behavior above 390 K: de-

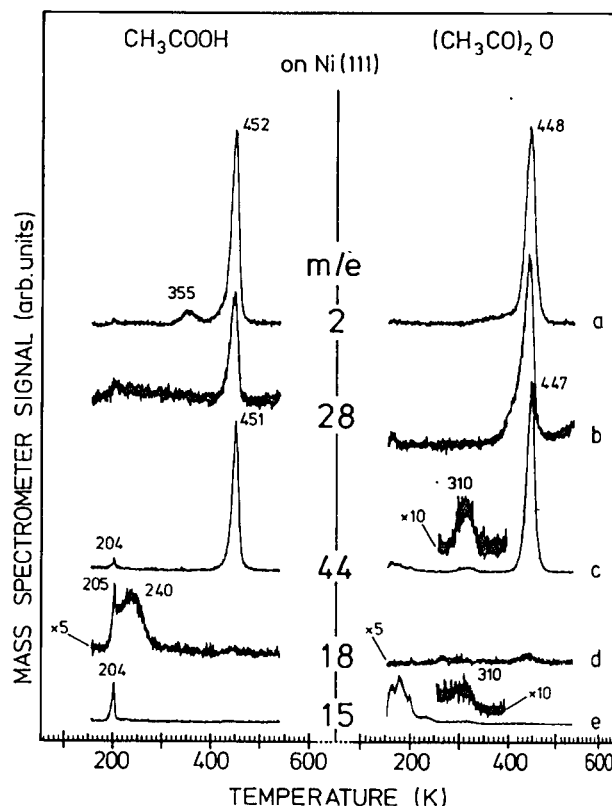


FIG. 1. Desorption spectra of masses 2, 28, 44, 18, and 15 taken after adsorption of acetic acid (left-hand side) and after adsorption of acetic anhydride (right-hand side) on a Ni(111) surface at 85 K. The heating rate was 1 K/s.

sorption maxima of hydrogen (mass 2), CO (mass 28), and CO₂ (mass 44) are observed near 450 K. This temperature is considerably higher than the corresponding temperature of 330 K reported for the decomposition of formic acid¹ on the Ni(111) surface, simply reflecting the higher stability of adsorbed acetic anhydride.

A small peak of hydrogen is observed at 355 K in cases of acetic acid but not in the case of the anhydride. This peak can be attributed to a small amount of adsorbed hydrogen,⁹ which is generated during the decomposition of acetic acid dimers. Desorption of water is observed for acetic acid as a relatively broad peak at 240 K, indicating a dehydration reaction similar to that observed for formic acid.¹ The sharp mass 18 and mass 44 peaks observed at 205 and 204 K, respectively, are associated with the cracking pattern of molecularly desorbing acetic acid. The same sharp peak is observed for the mass 15 peak (CH₃ fragments). As expected, no water desorption is observed in the corresponding spectrum of the acetic anhydride. Again, the mass 15 peak evolving around 200 K indicates the desorption of the excess physisorbed acetic anhydride.

For adsorbed acetic anhydride, Schoofs and Benziger⁷ reported additional weak desorption peaks of hydrogen and CO₂ around 300 K. In agreement with their findings, we too could detect small peaks around 310 K for the acetic anhydride but not for the acetic acid. However, as seen from Fig. 1(b), these mass 2 and 44 peaks at 310 K are of low intensity, and are substantially weaker than those previously report-

ed.⁷ This issue will be discussed below in connection with the IR results.

The experimental setup of the IR apparatus has been described in detail elsewhere.¹⁰ The total time for recording a spectrum was 4 min. All spectra were taken after cooling the sample to 85 K. Figure 2(a) shows the IR spectra of the surface intermediate in the frequency range from 1200–1600 cm⁻¹, which has been formed after heating an acetic acid covered Ni(111) surface to 250 K. No bands were detectable in the ranges below 1200 cm⁻¹ or above 1600 cm⁻¹. In particular, neither bands around 3000 cm⁻¹ due to CH stretching modes nor bands in the range 3300–3600 cm⁻¹ due to OH stretching modes are detectable. Whereas the latter, in accordance with EELS measurements on other surfaces, may indicate the rupture of the OH bond, the former is a result of the weak dynamic dipole moment of the CH bond as well as of the relatively poor signal-to-noise ratio of the instrument in that frequency range. Three different bands at 1447, 1435 and 1378 cm⁻¹ are well separated using an instrumental resolution of 4 cm⁻¹. The first two of these bands are assigned to CO stretching modes (see discussion below). In addition, a pronounced shoulder can be detected on the low frequency side of the 1435 cm⁻¹ band, which is located at 1424 cm⁻¹ when applying proper deconvolution [see dashed lines in Fig. 2(a)].

Figure 2(b) shows the IR spectra of adsorbed acetic anhydride after heating the Ni(111) sample to 320 K. By comparing the two spectra shown in Figs. 2(a) and 2(b), it becomes immediately evident that the frequencies of the corresponding bands do match nearly perfectly, although differences in the relative intensities of the bands exist. Heating the sample to 250 K causes only the emergence of the two most intense bands at 1447 and 1435 cm⁻¹, respectively. To obtain the two other bands at 1426 and 1378 cm⁻¹, the sample has to be annealed to above 320 K. This is in contrast to the acetic acid case, where all four bands are observed when dehydration is completed after heating to 280 K. The dashed line in Fig. 2(b) represents the convolution of the bands at 1447, 1435, 1424 and 1378 cm⁻¹ (Lorentzian line shapes) with an instrumental function (Gaussian line shape) of a full width at half maximum (FWHM) of 60 cm⁻¹, which represents a typical EELS instrumental function. As a result, none of the peaks is resolved and only a single broadband centered at 1425 cm⁻¹ is obtained exhibiting a slight asymmetry on the low frequency side due to the low frequency band at 1378 cm⁻¹. It should be noted that such a "single" vibrational band has been observed by EELS using an instrumental resolution between 60–80 cm⁻¹ after heating acetic acid adsorbed on Cu(100)^{2,3} (1430 cm⁻¹), Pt(111)⁴ (1400 cm⁻¹), and Al(111)⁵ (1470 cm⁻¹) surfaces to room temperature.

When using partially deuterated acetic acid (CD₃COOH), the IR spectrum of the intermediate, which is produced after heating the surface to 250 K, is shown in Fig. 3(a). The two major bands of the spectrum are now well separated and are only slightly shifted to lower frequencies at 1444 and 1424 cm⁻¹ when compared to the corresponding bands in the IR spectrum shown in Fig. 2(a) at 1447 and 1435 cm⁻¹, respectively. The two bands of weaker intensity

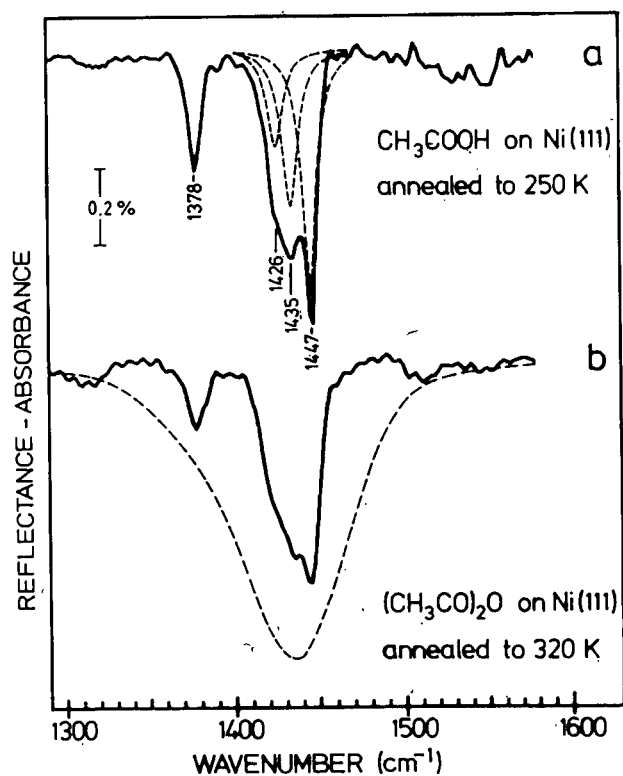


Fig. 2. IR spectrum taken after heating acetic acid to 250 K (a) and after heating acetic anhydride to 320 K (b), both priorly adsorbed on Ni(111) at 85 K. The dashed line in (b) represents the convolution of the IR bands with an EELS instrumental function of typical line width of 60 cm⁻¹.

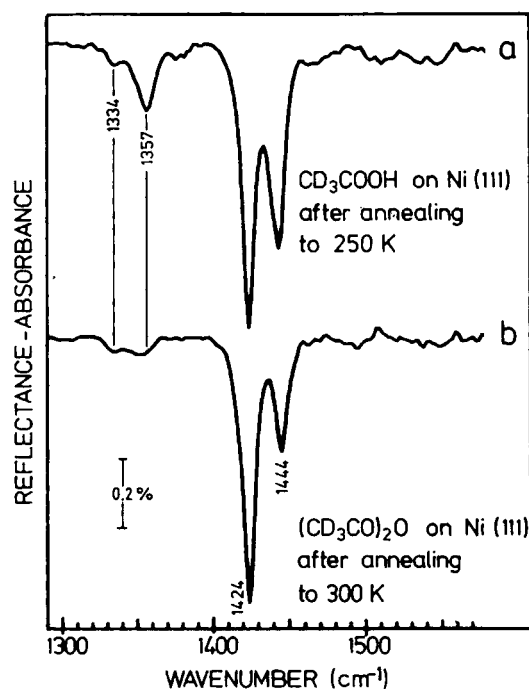


FIG. 3. IR spectrum taken after heating partially deuterated acetic acid to 250 K (a) and after heating perdeuteroacetic anhydride to 320 K (b), both priorly adsorbed on Ni(111) at 85 K.

observed at 1357 and 1334 cm^{-1} show a slightly stronger red shift when compared to the equivalent bands observed at 1424 and 1378 cm^{-1} , respectively [Fig. 2(a)]. Again, no bands due to CD stretching are observable around 2200 cm^{-1} , although the noise level in that frequency range is relatively low.

Figure 3(b) shows the IR spectrum obtained by heating the Ni(111) surface covered with perdeuteroacetic anhydride $(\text{CD}_3\text{O})_2\text{O}$ to 320 K. Again, aside from differences in intensities, all observed frequencies agree well with those shown in Fig. 3(a), and the two minor bands observed at 1357 and 1334 cm^{-1} only appear gradually when the sample is heated above 300 K. Considering the similarities between the spectra shown in Figs. 2(a) and 2(b) and those shown in Figs. 3(a) and 3(b), there remains little doubt that the species obtained by heating the acetic acid covered Ni(111) surface to 250 K and by heating the acetic anhydride covered surface to 320 K are identical. As in the case of adsorbed acetic anhydride, aside from the desorption of the molecular species below 200 K (indicated by the mass 15 cracking product), no other desorption products are observed when heated up to 300 K. Furthermore, no surface cracking products, e.g., CO, are detectable by IR spectroscopy in the temperature range up to 300 K. Hence, we conclude that the species observed by IR spectroscopy after heating the sample to 300 K is still due to adsorbed anhydride. Consequently, the intermediate formed after the dehydration of the adsorbed acetic acid at 250 K must be assigned to a surface anhydride.

The observation that all four bands show a small but clear red-shift upon deuteration leads to two conclusions: First, it

implies that hydrogen (deuterium) atoms are still attached to the surface intermediate, although no CH (CD) stretching bands are detectable in the IR spectrum above the noise level. Second, as the red-shift of the four bands is only 6% or less, none of these bands is assignable to CH bending modes as a much larger red-shift close to a factor of $\sqrt{2}$ should be expected.

The relatively strong intensity of the bands observed at 1447 and 1434 cm^{-1} , together with the small frequency shift to 1444 and 1425 cm^{-1} when using deuterated anhydride, identifies these two modes as the symmetric and asymmetric carbonyl stretching modes, respectively. Comparable small red-shifts upon deuteration have been reported for liquid acetic anhydride,¹¹ where the CO stretching modes shift from 1828 and 1756 cm^{-1} to 1823 and 1753 cm^{-1} , respectively. However, the considerable down-shift of the CO stretching bands by 320–380 cm^{-1} upon adsorption on the surface clearly indicates a reduction in the CO bond order.

The remaining two bands of lower intensities at 1426 and 1378 cm^{-1} [Fig. 2(b)] and 1357 and 1334 cm^{-1} for $(\text{CD}_3\text{O})_2\text{O}$ [Fig. 3(b)] could be assigned to the C–C–O–C skeletal modes of the adsorbed anhydride. Compared to the corresponding values of the liquid phase, these frequencies are substantially blue-shifted to higher frequencies. Such a blue-shift is a commonly observed feature for oxygen-containing hydrocarbons adsorbed at metal surfaces.⁵ Alternatively, these modes could be related to minority species, which may have formed by decomposition of the surface anhydride at surface defect sites. Some support for this idea is obtained from the observation of small desorption maxima of masses 15 and 44 in the TDS spectra [Figs. 1(c) and 1(d), right panel], peaking around 300 K. However, it should be noted, that the relative intensities of these peaks are considerably lower than those reported by Schoofs and Benziger.⁷

The strong bands due to the symmetric OCO bending mode are in all cases reported to appear below 800 cm^{-1} and are thus not accessible with our present IR apparatus (detector limited).

In summary, the results presented above clearly indicate that acetic anhydride, not the commonly predicted acetate, is the major reaction intermediate of the decomposition of acetic acid on Ni(111) surface. These results, combined with our previous observation of the formation of formic anhydride after the reaction of formic acid on Ni(111),¹ suggest that this class of organic molecules tend to form anhydride species on the Ni(111) surface.

¹W. Erley and D. Sander, *J. Vac. Sci. Technol. A* 7, 2238 (1989).

²B. A. Sexton, *Chem. Phys. Lett.* 65, 469 (1979).

³B. A. Sexton, *J. Vac. Sci. Technol.* 17, 141 (1980).

⁴N. R. Avery, *J. Vac. Sci. Technol.* 20, 592 (1982).

⁵J. G. Chen, J. E. Crowell, and J. T. Yates, Jr., *Surf. Sci.* 172, 733 (1986).

⁶A. Bowker and R. J. Madix, *Appl. Surf. Sci.* 8, 299 (1981).

⁷G. R. Schoofs and J. B. Benziger, *Surf. Sci.* 143, 359 (1984).

⁸R. J. Madix, J. L. Falconer, and A. M. Suszko, *Surf. Sci.* 54, 6 (1976).

⁹M. Hock and J. Küppers, *Surf. Sci.* 188, 575 (1987).

¹⁰W. Erley, *J. Electr. Spectr. Rel. Phen.* 44, 65 (1987).

¹¹P. Mirone, P. Fortunato, and P. Canziani, *J. Mol. Struct.* 5, 283 (1970).