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Infrared Study of the Adsorption of Formic Acid on Evaporated Nickel Film and Interaction of the Chemisorbed Species with Formic Acid

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The infrared spectra of HCOOH and DCOOD adsorbed on evaporated nickel film were measured in the 4000- to 400-cm^{-1} range and the reactivity of the adsorbed species was investigated.

Exposure of the nickel surface to HCOOH gave the five bands for the chemisorbed species at 2900, 1583, 1390, 1345, and 795 cm^{-1} as well as for the physically adsorbed species at 1715 cm^{-1}. The chemisorbed species of DCOOD gave the bands at 2180, 1575, 1060?, 1325, and 780 cm^{-1}.

The chemisorbed species is assigned to $(\mathrm{HCOO}^-)_{\mathrm{ads}}$. The chemisorbed $(\mathrm{HCOO}^-)_{\mathrm{ads}}$ did not change through the exposure of D_2 but it was easily displaced by the $(\mathrm{DCOO}^-)_{\mathrm{ads}}$ upon addition of DCOOD at room temperature. The changes in the spectra of the adsorbed species caused by heating were studied. The results are discussed in relation to the mechanism of the dehydrogenation reaction of formic acid by metal catalysts and the formation of an intermediate complex from $(\mathrm{HCOO}^-)_{\mathrm{ads}}$ and $(\mathrm{HCOOH})_{\mathrm{ads}}$ is proposed.

INTRODUCTION

Infrared studies of the adsorption of gases on various surfaces have provided much interesting information. Especially Eischens and co-workers (*1*) have demonstrated a wide applicability of infrared techniques to the study of catalysis; they worked, however, mainly with silica-supported metals. Because of a large infrared absorption by the silica support, however, the available range for the infrared studies is restricted, and investigations in the far-infrared region have been unsuccessful. Blyholder (*2*) has obtained the infrared spectra of adsorbed species in the 5000 to 270 cm^{-1} range on evaporated metal particles, which were deposited on cesium bromide windows coated with oil. The use of oil in his method, however, makes it impossible to heat the catalyst and also to obtain the bands caused by the vibration of the carbon–hydrogen bonds of the adsorbed species. To avoid these difficulties, a modification of the technique was developed and it was applied to the study of the catalytic decomposition of formic acid into hydrogen and carbon dioxide. Recently Garland, Lord, and Troiano (*3*) studied chemisorption problems on various metals which were evaporated on salt windows.

The dehydrogenation reaction proceeds on various metals, as has been found by many authors. In the course of this reaction, a kind of formate ion has been concluded to exist from the studies of kinetic isotope effects (*4, 5, 6*), isotope distribution of the products (*7*), infrared spectra of adsorbed species (*7–10*), and decomposition products of the adsorbed species (*11*). Several authors suggested this adsorbed formate ion to be a reaction intermediate. The way in which the adsorbed species reacts, however, has not been clarified.

In order to have more definite information about the mechanism of the catalytic decomposition of formic acid, the infrared spectra of HCOOH and DCOOD adsorbed on nickel films, as well as the effects of formic acid and deuterium gas on the adsorbed species, are investigated over the range from 4000 to 400 cm^{-1} by the use of a new cell. A new intermediate complex composed of formate ion and formic acid is suggested as the intermediate of the exchange and the dehydrogenation reactions of the adsorbed species.

EXPERIMENTAL

The cell used is shown in Fig. 1. Nickel was evaporated from a tungsten filament on three KBr disks in a vacuum cell equipped with KBr windows. These three KBr disks were supported inside the cell by tungsten wire. The windows were secured to the cell with glyptal resin. The tungsten filament with a thin nickel wire wound around it was inserted in the cell by means of taper joint which was sealed with high-vacuum grease.

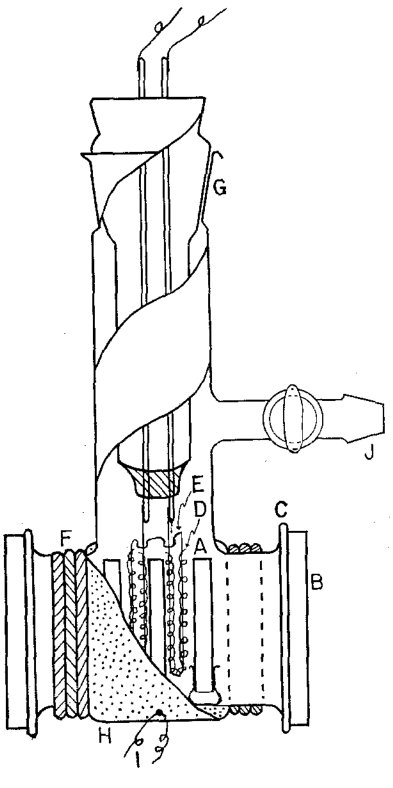

FIG. 1. Diagram of the cell. A, KBr disks; B, KBr windows; C, ground glass; D, thin metal wire; E, tungsten heater; F, cooling copper wire; G, taper joint; H, asbestos; I, thermocouple; J, taper joint to vacuum system.

The cell was then kept under a vacuum of 10^{-3} mm Hg for a day, followed by about 3 hr of evacuation at about 10^{-5}-mm pressure. After 15 min of preheating of the tungsten filament for degassing the filament and the nickel wire, nickel was evaporated onto four planes of KBr disks in about 30 sec. The result was a very thin porous film of nickel which reduced the infrared transmission down to about 40%. Further evaporation made films opaque (*3*) and did not increase the infrared band intensity produced by the adsorbed species. Wire gauges were inserted in the reference beam to raise the apparent transmission. The evaporated films could be heated by the same tungsten filament as used for the evaporation. Both ends of the cell were equipped with copper cooling wires. This allowed the catalyst to be heated to about 150°C without glyptal resin flowing onto the windows. The temperature was measured by a thermocouple outside the cell as shown in Fig. 1.

Spectra were recorded on a Nippon Bunko (Japan Spectroscopic) Model DS-402G infrared spectrophotometer and the scanning speed was about 45 min from 4000 to 700 cm^{-1}.

The formic acid used was a Wako Pure Chemicals product, which was fractionally distilled in vacuum after repeated drying with anhydrous copper sulfate. DCOOD was prepared by the thermal decomposition of deuterated oxalic acid. The percentage of D of the hydrogen bonded to carbon was about 80%. Nickel formate was prepared by the reaction of nickel carbonate with formic acid. Deuterium gas (99%) was obtained from Takachiho Chemical Industrial Co.

RESULTS

Preliminary experiment. A spectrum of gaseous formic acid (30 mm Hg) was recorded using the cell with preheated KBr disks, but without any nickel film on them. This was identical with the known spectrum of gaseous formic acid, and the absorption bands completely disappeared after half an hour of evacuation. No interaction between formic acid and potassium bromide was therefore shown in the spectrum.

Formic acid adsorption. The infrared spectra recorded after the nickel film was exposed to formic acid vapor (30 mm Hg)

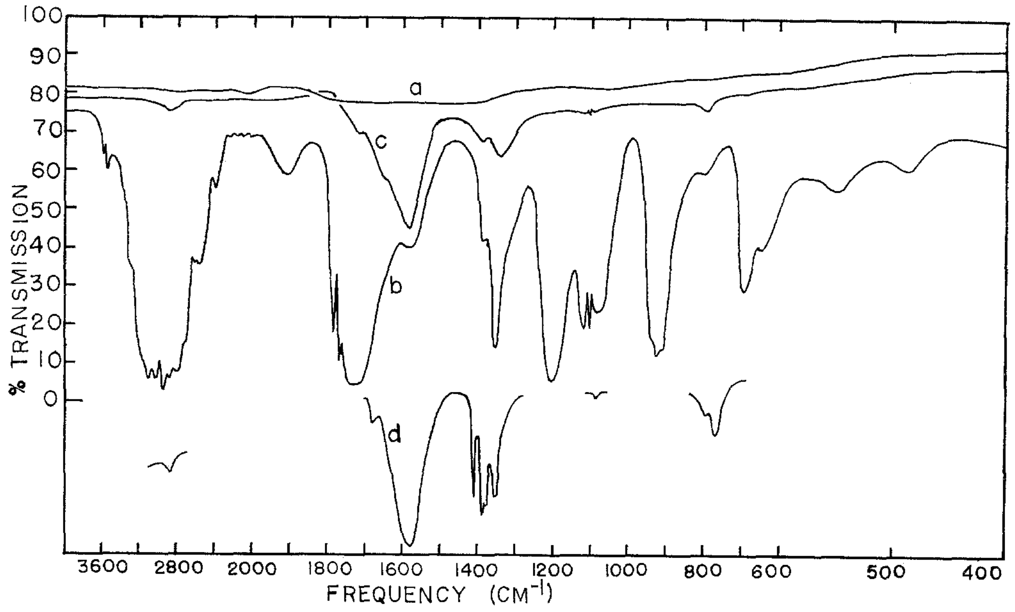

FIG. 2. Spectra of formic acid adsorbed on nickel film at room temperature: (a) background spectrum of nickel film; (b) spectrum with 30 mm Hg of HCOOH in cell; (c) after an hour of condensation of gaseous formic acid; (d) spectrum of nickel formate for comparison.

are shown in Fig. 2, in which the spectrum (a) is the background of the nickel film and spectrum (b) is the one recorded 30 min after the gas was introduced into the cell at room temperature.

Then the formic acid vapor was condensed by a liquid nitrogen trap. The intensity of the bands due to the vapor decreased immediately, while the band at 1715 cm^{-1} decreased gradually, which indicates the presence of HCOOH on the nickel surface. The spectrum (c), recorded after an hour of trapping by liquid nitrogen, shows the bands of the adsorbed formic acid. When the sample was heated at 80°C after an hour of trapping, the bands at about 1715 cm^{-1} disappeared. The bands at 2900, 1583, 1390, 1345, and 795 cm^{-1}, however, did not change after 2 hr of heating at 80°C, though their intensities began to decrease when the sample was heated up to 120°C. Hence these five bands were assigned to the chemisorbed species. After cooling the sample to room temperature, a spectrum identical with (b) was observed again by addition of formic acid. This means that the decrease of the band intensity after heating to 120°C was not due to the exfoliation of the nickel from the KBr plate. DCOOD adsorption on nickel also gave a qualitatively similar result as HCOOH adsorption.

The bands obtained after trapping of formic acid vapor are summarized in Table 1, each with the corresponding mode of vibration. Besides, the spectra of formate ion in aqueous solution (*11*), sodium formate (*12*) and nickel formate are shown for the sake of comparison. The spectrum of nickel formate is shown as the spectrum (d) in Fig. 2.

Interaction of the chemisorbed species with deuterium gas. The spectrum caused by the chemisorbed species was observed after the nickel film was exposed to HCOOH vapor (30 mm Hg) at room temperature and the cell was evacuated for 2 hr. Then 18 mm of D_2 was introduced in the cell. No change was observed in the spectrum even when the sample was heated at 70°C for an hour.

Interaction of the chemisorbed species with formic acid. The spectra were recorded when HCOOH and DCOOD were added to the nickel film alternately and are shown in Fig. 3. First, 30 mm of HCOOH

TABLE 1

THE INFRARED BANDS OF ADSORBED SPECIES AND FORMATE ION[a]

Physically adsorbed species: 1715					
Chemisorbed formate ion					
$(HCOO^-)_{ads}/Ni$	2900	1583	1390	1345	795
$(DCOO^-)_{ads}/Ni$	2180	1575	1060?	1325	780
Formate ion in solution[b]					
$HCOO^-$	2825	1585	1385	1351	772
$DCOO^-$	2122	1580	1028	1329	755
Sodium formate[c]	2841	1567	1377	1366	772
Nickel formate	2905	1580	1402, 1383	1375, 1356	798,770
Assignment[c]	ν(C–H)	ν_a(COO)	ν(CH) in-plane	ν_s(COO)	δ(COO)

[a] In cm^{-1}.

[b] Reference 12.

[c] Reference 13.

was added to the fresh nickel surface at room temperature and the spectrum was recorded. The formic acid vapor then was removed by condensing it by liquid nitrogen trap for an hour. The resulting spectrum is curve (a), which shows the bands of $(HCOO^-)_{ads}$. After that 30 mm of DCOOD was added to the sample at room temperature, and the spectrum was obtained. The vapor then was trapped again by liquid nitrogen for an hour and the spectrum (b) was recorded, in which the bands of the chemisorbed $(DCOO^-)_{ads}$ were obtained instead. Upon subsequent addition of HCOOH (30 mm Hg), the spectrum (c) corresponding to $(HCOO^-)_{ads}$ was again observed.

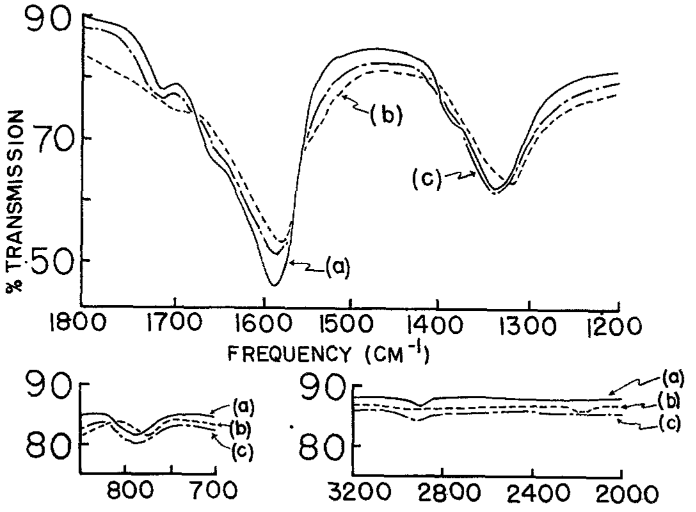

FIG. 3. Interaction of adsorbed species and formic acid on nickel film: (a) spectrum of chemisorbed species by HCOOH adsorption; (b) spectrum of chemisorbed species after addition of DCOOD on $(HCOO^-)_{ads}$; (c) after subsequent addition of HCOOH on $(DCOO^-)_{ads}$.

DISCUSSION

Formic acid adsorption on nickel film. Since the infrared spectra revealed no interaction between formic acid and potassium bromide, the spectrum (c) shown in Fig. 2 is concluded to arise from the adsorbed species. The band at 1715 cm^{-1} decreased in intensity by heating at 80°C and thus it is assigned to the physically adsorbed species (7–10). The above results indicate that formic acid was adsorbed physically on the nickel without silica support. The five bands at 2900, 1583, 1390, 1345, and 795 cm^{-1} which remained after the heating at 80°C are considered to arise from the chemisorbed species and are assigned to the adsorbed formate ion by comparison of them with the spectra of various formates, listed in Table 1. The band at 795 cm^{-1} corresponds to the band at 770 cm^{-1} observed on zinc film in our earlier work (*14*). The frequencies of the other bands agree with those which were reported on various metals including nickel, and have already been assigned to the formate ion. The band due to the C–H out-of-plane bending vibration was not observed, perhaps because of its weak intensity. According to the above interpretation of the chemisorbed species, it would be expected that the use of DCOOD or DCOOH would result in an adsorbed deuterated formate ion. The band shifts of the chemisorbed formate ion caused by deuteration were observed actually as shown in Table 1, and they correspond to those of formate ion in aqueous solution, confirming the present assignment for adsorbed species.

Eischens and Pliskin (*15*) studied the spectra of HCOOH and DCOOD chemisorbed on Ni at -60°C, and obtained the bands at 2941, 1587, 1359 cm^{-1} for HCOOH and 2188, 1546, and 1325 cm^{-1} for DCOOD, respectively, but they assigned them to the covalently chemisorbed species. Recently, Rooney and Webb (*16*) proposed the same state, assuming a π-bonded intermediate. The infrared spectra of various formates were reported, but no remarkable tendency by the difference of their bond character is found in the spectra above 700 cm^{-1}. Therefore, the degree of covalency of the bond between the chemisorbed formate ion and the nickel could not be decided on the basis of infrared spectra in the range from 4000 to 700 cm^{-1}. The chemisorbed species, therefore, is conveniently represented by $(HCOO^-)_{ads}$, and this notation does not mean that the bond between catalyst and formate is perfectly ionic. Spectra in the far-infrared region are necessary so as to determine this bond character finally.

The bands of the chemisorbed species were reduced in intensity on heating up to about 120°C, but not at 80°C. This finding suggests that the chemisorbed species begin to decompose at about 120°C by themselves but not at about 80°C. In other words, the following reaction is not observed at about 80°C:

$$2(HCOO^-)_{ads} \rightarrow H_2 + 2CO_2$$

Interaction of the chemisorbed species and deuterium gas. It was found that the chemisorbed $(HCOO^-)_{ads}$ was stable to 18 mm of D_2 at 70°C. This result shows that the following reactions would not occur under the present conditions:

$$(HCOO^-)_{ads} \xrightarrow{D_2} HCOOD$$

$$(HCOO^-)_{ads} \xrightarrow{D_2} HD + CO_2$$

Interaction of the chemisorbed species with formic acid. Addition of HCOOH, DCOOD, and HCOOH in this order resulted in the appearance of the spectra of $(HCOO^-)_{ads}$, $(DCOO^-)_{ads}$, and $(HCOO^-)_{ads}$ successively. This finding indicates that the chemisorbed species is unstable in the presence of the vapor or the physically adsorbed species of formic acid. This instability is ascribable to the decomposition of formate ion and/or the desorption as formic acid. The band intensity of the physically adsorbed species was reduced by the trapping by liquid nitrogen at room temperature, but those of chemisorbed $(HCOO^-)_{ads}$ were not changed. Hence, a rapid equilibration $(HCOO^-)_{ads} + (H^+)_{ads} \rightleftharpoons (HCOOH)_{ads}$ could not be expected and the sites for chemisorption on nickel surface are considered to be almost occupied in the present experimental condition. Therefore, upon addition of HCOOH over $(DCOO^-)_{ads}$, physically adsorbed formic acid is considered to compose an adsorbed intermediate complex with $(DCOO^-)_{ads}$, and this complex takes part in the exchange and the decomposition reaction.* Namely, the following reactions are expected:

$$\begin{array}{ccccc} (HCOOH)_{ads} & \rightleftharpoons & \text{Intermediate} & \rightleftharpoons & (HCOO^-)_{ads} \\ +\ (DCOO^-)_{ads} & & \text{complex} & & +\ (DCOOH)_{ads} \\ & & \downarrow & & \\ & & CO_2 + HD + (HCOO^-)_{ads} & & \\ \text{or} & & CO_2 + H_2 + (DCOO^-)_{ads} & & \text{(a)} \end{array}$$

In the above discussion, $(HCOOH)_{ads}$ does not necessarily lie on nickel atoms directly.

Reaction scheme of the dehydrogenation of formic acid on nickel film. Many authors concluded from various information that the reaction intermediate $HCOO^-$ takes part in the dehydrogenation reaction of formic acid on nickel. A more detailed discussion is made in this paper on the mechanism of the reaction, considering the present results.

Block and Kral (*4*), Otaki (*5*), and Watson (*6*) measured the kinetic isotope effect in the dehydrogenation of HCOOH, HCOOD, DCOOH, and DCOOD on Ag, Au, Cu, and Pd catalysts and found the following results in the reaction rate (r): $r_{HCOOH} > r_{HCOOD} > r_{DCOOH} > r_{DCOOD}$. The reaction step which determines the reaction rate, therefore, must include two or more activated H atoms. Hirota and co-workers (*7*) studied the isotope distribution in the decomposition products of deuterated formic acid and observed that the amount of HD produced in the decomposition of HCOOD or DCOOH on Ag film was much larger than would be expected from the equilibration of the reaction $H_2 + D_2 = 2HD$. Furthermore the rate of this equilibration was found to be negligible under the conditions used. This finding suggests that all the dehydrogenation reactions occur neither in a monomolecular reaction nor in the following reaction: $2(HCOO^-)_{ads} \rightarrow H_2 + 2CO_2$.

In order to explain the results of the kinetic isotope effect and the isotope distribution of the dehydrogenation products of deuterated formic acid, the following reaction scheme was tentatively proposed for the reaction under zero order with the assumption that the reaction scheme on nickel is the same as that on silver:

$$HCOOH \rightarrow (HCOO^-)_{ads} + H^+_{ads} \qquad \text{(I)}$$

$$\begin{array}{ccccc} (HCOO^-)_{ads} & \rightleftharpoons & \text{intermediate} & \rightleftharpoons & (HCOOH)_{ads} \\ +\ (HCOOH)_{ads} & & \text{complex} & & +\ (HCOO^-)_{ads} \\ & & \downarrow & & \\ & & H_2 + CO_2 + (HCOO^-)_{ads} & & \text{(IIa)} \end{array}$$

$$2(HCOO^-)_{ads} \rightarrow H_2 + 2CO_2 \qquad \text{(IIb)}$$

$$2H^+_{ads} \rightarrow H_2 \qquad \text{(III)}$$

The adsorbed state of hydrogen is tentatively denoted by H^+_{ads}, but it may be a proton, a hydrogen atom, a surface hydride, or their mixed state. The formate ion is formed first, the step (IIa) then mainly proceeds in the dehydrogenation and the step (IIb) proceeds as side reaction, especially at higher temperature. The steps (IIa), (IIb), and (III) would give the above isotope distribution of the decomposition products, and the kinetic isotope effect could be explained if the step (IIa) mainly determines the decomposition rate. In this reaction scheme, if the number of the $(HCOOH)_{ads}$ that can compose the intermediate complex with $(HCOO^-)_{ads}$ was constant, the reaction order would be zero at high pressure and low temperature. But this does not mean that all the physically adsorbed species play the role of the intermediate complex.

The above discussion is valid no matter whether the formate is ion or radical. In order to discuss in more detail the dehydrogenation mechanism of formic acid on nickel, direct evidence of step (IIa) is desirable.

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REFERENCES

1. EISCHENS, R. P., AND PLISKIN, W. A., *Advan. Catalysis* **10**, 1 (1958).

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* The dehydrogenation of formic acid at room temperature was observed by Sachtler and coworkers (*9*b). The decomposition products were analyzed on nickel at 19°C after the reaction gas had been rapidly removed from the catalyst by flushing with formic acid and it was found that the ratio of CO and CO_2 was 0.250.

2. Blyholder, G., *J. Chem. Phys.* **36**, 2036 (1962).
3. Garland, C. W., Lord, R. C., and Troiano, P. F., *J. Phys. Chem.* **69**, 1188 (1965).
4. Block, J., and Kral, H., *Z. Elektrochem.* **63**, 182 (1959).
5. Otaki, T., *J. Chem. Soc. Japan* **80**, 255 (1959).
6. Watson, A. M., Inaugural Dissertation, Ludwig-Maximilians-Universität zu München, 1962.
7. Hirota, K., Kuwata, K., Otaki, T., and Asai, S., *Actes Congr. Intern. Catalyse, 2e, Paris, 1960,* p. 809 (Edition Technip, Paris, 1961).
8. (a) Hirota, K., Kuwata, K., and Nakai, Y., *Bull. Chem. Soc. Japan* **31**, 861 (1958); (b) Hirota, K., Otaki, T., and Asai, S., *Z. Physik. Chem. (Frankfurt)* **21**, 438 (1959).
9. (a) Fahrenfort, J., and Hazebroek, H., *Z. Physik. Chem. (Frankfurt)* **20**, 105 (1959); (b) Fahrenfort, J., van Reijen, L. L., and Sachtler, W. M. H., "The Mechanism of Heterogeneous Catalysis" (J. H. de Boer, ed.), p. 23. Elsevier, Amsterdam, 1960.
10. Clarke, J. K. A., and Pullin, A. D. E., *Trans. Faraday Soc.* **56**, 534 (1960).
11. Tamaru, K., *Trans. Faraday Soc.* **55**, 824 (1959).
12. Landolt-Börnstein, "Zahlenwerte und Funktionen," Vol. I, Part 2, p. 237. Springer, Berlin, 1951.
13. Ito, K., and Bernstein, H. J., *Can. J. Chem.* **34**, 170 (1956).
14. Ogawa, T., Kishi, K., and Hirota, K., *Bull. Chem. Soc. Japan* **37**, 1306 (1964).
15. Eischens, R. P., and Pliskin, W. A., *Actes Congr. Intern. Catalyse, 2e, Paris, 1960,* p. 789 (Edition Technip, Paris, 1961).
16. Rooney, J. J., and Webb, G., *J. Catalysis* **3**, 488 (1964).