*Infrared Spectra of Adsorbed Formic Acid**

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In order to investigate the mechanism[1] of the catalytic decomposition of formic acid, the infrared spectra of adsorbed formic acid have been already studied by Hirota, Kuwata and Nakai,[2] and by others[3]. Hirota et al. found new bands at 1590 cm^{-1} and 1360 cm^{-1} for the silica-supported zinc catalyst[2] and assigned these bands to the chemisorbed formate anion.

The adsorbent hitherto investigated have, however, been confined to the metal oxides and supported metals, and their spectral region has usually been in the range from 2000 cm^{-1} to 1250 cm^{-1}.[2] In order to clarify the reaction mechanism, a spectroscopic study of the adsorbed state on pure metals and an extension of the wavelength region have to be carried out. In the present report, a new cell for infrared measurement is devised and adsorbed states on evaporated metal films are investigated in the four ranges from 4000 cm^{-1} to 400 cm^{-1}.

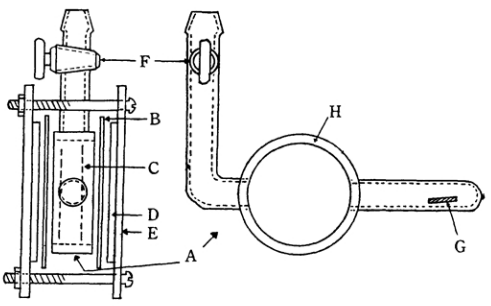

Fig. 1. Diagram of the cell.
A, hard glass cell; B, polyethylene window; C, polyethylene substratum; D, rubber sheet; E, brass holder; F, stopcock; G, zinc metal; H, ground glass

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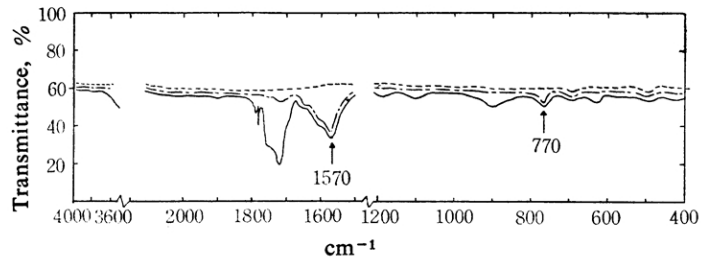
1) Cf. "Advances in Catalysis and Related Subjects," Vol. 14, Academic Press, New York (1963), p. 35.

2) K. Hirota, K. Kuwata and Y. Nakai, This Bulletin, **31**, 861 (1958); K. Hirota, K. Kuwata and S. Asai, *J. Chem. Soc. Japan, Pure Chem. Sec. (Nippon Kagaku Zasshi)*, **80**, 701 (1959); K. Hirota, T. Otaki and S. Asai, *Z. physik. Chem. N. F.*, **21**, 438 (1959).

3) J. Fabrenfort and H. F. Hazebroek, ibid., **20**, 105 (1959); T. K. A. Clarke and A. D. E. Pullin, *Trans. Faraday Soc.*, **56**, 534 (1960).

4) Landolt-Börnstein, Table I, 2, p. 237 (1957); Cf. K. Ito and H. J. Bernstein, *Can. J. Chem.*, **34**, 170 (1956).



Fig, 2. Spectra of formic acid on evaporated zinc film at room temperature. Two bands of adsorbed state are indicated by arrows.
—— at 30 mmHg of HCOOH.
–·– after an hour's evacuation.
---- background spectrum of zinc film.

TABLE I. THE INFRARED SPECTRA OF FORMATE ANION AND ADSORBED SPECIES

	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6
Adsorbed formate; present study			770	1570		
Adsorbed formate; by Hirota et al.[2]		1360		1590	1360	
Zinc formate; present study	2900?	1355	767	1580	1380	1075?
Formate ion in solution[6]	2803	1351	760	1585	1383	1069
Assignment	ν(CH)	ν(CO)	δ(OCO)	ν(CO)	δ(CH)	δ(CH)

Experimental

The cell was made of hard glass, on which windows of polyethylene films 0.5 mm. thick were stuck with a small amount of glyptal resin, as is shown in Fig. 1. Similar films 0.1 mm. thick were set in the cell as substrata for the evaporated metal film. The cell was then degassed and kept under about 10^{-2} mmHg for several days. The use of polyethylene as optical windows made it possible to measure the 4000 cm^{-1}~3100 cm^{-1}, 2500 cm^{-1}~1500 cm^{-1}, 1250 cm^{-1}~750 cm^{-1} and below 700 cm^{-1} regions. Zinc metal could easily be evaporated on the thin polyethylene films by heating it externally with a gas-burner.

The spectra were recorded with a Nippon Bunko Model DS402G spectrometer. Polyethylene films and a wire netting were inserted in the reference beam during the measurement. Formic acid was dried by anhydrous cupric sulfate.

Results and Discussion

The spectrum of the evaporated zinc film was measured first, and then formic acid was introduced into the cell at about 30 mmHg. The two spectra are shown in Fig. 2 by a dotted and a solid line respectively. Successive evacuation and spectral measurements were carried out; one of such spectra is shown in the figure by a dot-dash line.

The observed bands are summarized in Table I. The bands which disappeared after ten minutes' evacuation were assigned to formic acid in the vapor state. The two band which remained after an hour's evacuation were considered to arise from the chemisorbed species and were assigned to the adsorbed formate anion on the basis of a comparison of them with the spectra of the zinc formate and the formate anion in solution.

The effects of polyethylene or glyptal resin on the adsorbed state were checked; no band of the formate anion or others was observed without the metal film after ten minutes' of pumping. The saturated hydrocarbon as polyethylene is chemically inactive and is considered to have less influence on the adsorbed states than does a silica or alkali halides crystal. The present method, therefore, not only makes it possible to find a new band at 770 cm^{-1}, but also reveals the less unperturbed adsorbed states.

Summary

The infrared spectra of adsorbed formic acid on zinc have been measured. Two bands have been found at 1570 cm^{-1} and 770 cm^{-1} and assigned to the adsorbed formate anion.

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