Studies on the State of Formic Acid Adsorbed on Silica and Alumina by a Combined Method of Nuclear Magnetic Resonance and Infrared Absorption

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As reported already[1], formic acid is chemisorbed as the formate ion on several metallic powders (Ag, Cu, Ni, Rh, Pd, Pt and Zn), while the acid chemisorbed on silica does not dissociate[2]. However, it was found in the present study that the conclusion obtained in the case of silica can not be applied to alumina, especially in the case of low coverage of adsorption. Such a conclusion may be worthy to be reported, considering the fact[3] that the catalytic role of alumina is similar to that of silica rather than that of metals, e. g., these oxides have dehydrating activity in addition to dehydrogenating activity, contrary to the case of metals which have only dehydrogenating activity.

Experimental

Formic Acid.—The reagent of C. P. grade made by Edogawa Kagaku Kogyo Co. was repeatedly dehydrated by crystallization and then vacuum-distilled in the presence of anhydrous copper sulfate.

Silica.—Silica gel for chromatographic use made by Mallinkrodt Chemical Works was dehydrated at 300°C for 150 hr. It was confirmed by X-ray analysis that the amorphous structure of silica was not changed by dehydration. The specific surface area of the silica was found to be 520 m^2/g. by the BET method (adsorbate: nitrogen).

Alumina.—Alumina gel, precipitated by the reaction between aluminum nitrate and ammonia in aqueous solution, was dehydrated at 300°C for 50 hr. The specific surface area was found to be 310 m^2/g.

Measurement.—Formic acid was adsorbed on each adsorbent which was enclosed in a glass sample tube in vacuo. In the case of nuclear magnetic resonance measurement, a capillary tube filled with water as a standard substance was put in the center of the sample tube. The proton resonance spectra were obtained with a high resolution spectrometer (Varian V-4300B)* at a fixed frequency of 40 Mc/sec. The tube was always rotating around its axis during the measurement. The infrared spectra were obtained using the paste method[4], in which the sample was quickly mulled with Nujol, and a part of the sample was held between the plates of sodium chloride and then offered for measurement (apparatus: Hilger H800). During this procedure a small amount of formic acid may be lost in the atmosphere, but it was checked that this amount was small enough not to alter the conclusion. Taking such a situation into account, the coverage was conventionally designated by θ' instead of the true coverage θ in the case of samples used in infrared absorption measurement. Measurements were made at room temperature.

Results and Discussion

Proton Magnetic Resonance Absorption.—The proton resonace spectrum of formic acid

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[1] 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).

[2] K. Hirota, K. Fueki, K. Shindo and Y. Nakai, This Bulletin, **31**, 783 (1958).

[3] G. M. Schwab and E. Schwab-Agallidis, *J. Am. Chem. Soc.*, **71**, 1806 (1949).

* In the preliminary report, the apparatus was referred to as Varian V-4310C, because some part of the apparatus is so named.

[4] G. C. Pimentel, C. V. Gerland and G. Jura, *J. Am. Chem. Soc.*, **75**, 803 (1953).

adsorbed on silica is quite different from that in the liquid state, especially when the amount of adsorption is small, (e. g., $\theta=0.5$); only one signal**, corresponding to the hydrogen atom bonded to the carbon atom, appears as a broad one and, moreover, its position shifts by 33 cps to a higher magnetic field. However, as the coverage is increased up to 2.7, the signal becomes narrower in width and that of the hydrogen atom bonded to the oxygen atom also appears as a very broad one. Thus it may be concluded that the motion of hydrogen in the carboxyl group is fixed in the state of monomolecular adsorption, and such a restriction of the motion is relaxed gradually according as the adsorption layer is the upper. Furthermore, it is pointed out that the observed shifts may be mainly of apparent nature, and therefore, the effect of the magnetic susceptibility of bulk substance was taken into consideration. The chemical shifts, corrected for this effect[5], are shown in the last column of Table I. Though it seems that there is a relation between the amount of adsorbed formic acid and the chemical shift, it is too small for the meaning to be discussed in detail.

TABLE I. CHEMICAL SHIFT OF FORMIC ACID ADSORBED ON SILICA***

(Unit: cps)

δ_{ads}: Shift from reference (water)
δ_{meas}: Shift from liquid formic acid
δ_{cor}: Value to be corrected for bulk magnetic susceptibility
$\delta=\delta_{meas}-\delta_{cor}$: Chemical shift

θ	δ_{ads}	δ_{meas}	δ_{cor}	δ
0.5	97	33	26	7
1.1	100	30	25	5
1.7	103	27	23	4
2.7	109	21	19	2

On the other hand, we could not detect any appreciable signal for the formic acid adsorbed on alumina in the monomolecular state. This is probably due partly to the small amount of adsorption and partly to stronger interaction with alumina than with silica.

Furthermore, the difference in the adsorbed state between silica and alumina could be made clear by the infrared absorption measurement as shown below.

Infrared Absorption.—*Silica.*—In the case of silica two adsorption bands are observed at 3450 (broad) and $1620\ \mathrm{cm}^{-1}$. Both bands may be ascribed to associated water on the surface[6]. However, the stretching band due to the isolated hydroxyl group on the silica surface[7] does not appear at $3749\ \mathrm{cm}^{-1}$, probably being masked by the broad band at $3450\ \mathrm{cm}^{-1}$[8].

Now, when formic acid is adsorbed on silica, new absorption bands appear at 1714 and $960\ \mathrm{cm}^{-1}$ in addition to the band near $3520\ \mathrm{cm}^{-1}$ (Fig. 1, Table II). The absorption band at $1714\ \mathrm{cm}^{-1}$ can be ascribed to the C=O stretching vibration, while the band at $960\ \mathrm{cm}^{-1}$ to the OH out-of-plane deformation vibration. Thus, it may be said that formic acid is adsorbed on silica in a non-dissociated state. The C=O stretching band shifts to lower frequency as compared to that of the monomer and also of the dimer. This band is rather similar in frequency to that of formic acid in the crystalline state. The same situation holds for the OH deformation band[9]. Considering these facts, it seems that the adsorbed formic acid forms hydrogen bonding not only to the silica surface, but also to each other, forming thus a two-dimensional net structure. Such a model

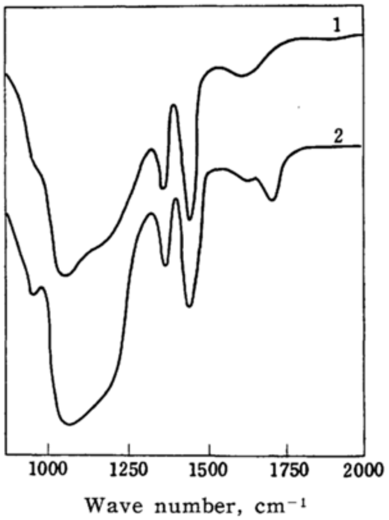

Fig. 1. Infrared spectrum of formic acid adsorbed on silica.
1: silica, 2: $\theta'=0.7$

** The assignment of the signal was made by the use of deuteroformic acid HCOOD.

5) J. R. Zimmerman and M. R. Foster, *J. Phys. Chem.*, **61**, 282 (1957).

*** The resonance of proton bonded to the carbon atom is shown.

6) A. Chevet, *J. Phys. Radium*, **14**, 493 (1953).

7a) R. S. McDonald, *J. Am. Chem. Soc.*, **79**, 850 (1957); *J. Phys. Chem.*, **62**, 1168 (1958).

b) A. N. Terenin, N. G. Yaroslavskii, A. V. Karyakin and A. I. Sidorova, *Microchim. Acta*, 467 (1955).

8) K. Naito, presented at the Symposium on Infrared and Raman Spectra, Kyoto, October, 1958.

9) R. C. Millikan and K. S. Pitzer, *J. Chem. Phys.*, **27**, 1305 (1957); *J. Am. Chem. Soc.*, **20**, 3515 (1958).

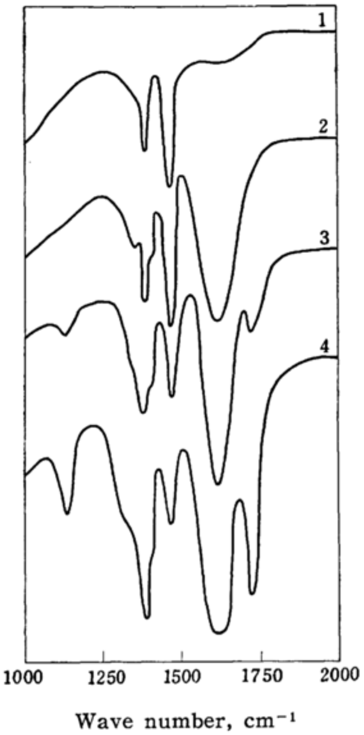

Fig. 2. Infrared spectrum of formic acid adsorbed on alumina.
1: alumina, 2: $\theta'=0.7$, 3: $\theta'=1.3$, 4: $\theta'=2.4$.

was already proposed in the case of the adsorption of water and ethanol on silica from the results of the dielectric measurement of these systems[10,11].

Alumina. — In the infrared spectrum of alumina, not only the absorption bands (3450 and 1620 cm^{-1}) of associated water on the surface, but also that (3760 cm^{-1}) of the isolated hydroxyl group are observed. When formic acid is adsorbed in a monomolecular layer, new absorption bands appear at 1344 and 1402 cm^{-1} besides 1620 cm^{-1} (strong), while the intensity of the band at 3450 cm^{-1} does not vary (Fig. 2, Table II). As the bands at 1344, 1402 and 1620 cm^{-1} can be assigned to the fundamental modes of vibration, ν_2, ν_5 and ν_4, of the formate ion[12], respectively, the state of formic acid adsorbed on alumina is similar to that on metals. However, when the amount of adsorbed formic acid is increased and a monomolecular layer is completed, new absorption bands appear at 1733 and 1124 cm^{-1}, and the band near 3520 cm^{-1} increases in intensity. These results show that non-dissociated formic acid can exist in the upper layer of adsorption on alumina.

TABLE II. SUMMARIZED RESULTS OF INFRARED ABSORPTION****

Adsorbent	θ'			
	0.3	0.7	1.3	2.4
Silica	1714 960	1714 960	1714 960	— —
Alumina			1733 (1705)	1733 (1705)
	1620 (1602)	1620 (1602)	1620 (1602)	1620 (1602)
	1402 (1377)	1402 (1377)	1402 (1377)	1402 (1377)
	1344 (1329)	1344 (1329)	1344 (1329)	1344 (1329)
			1124 (1100)	1124 (1100)

In short, it has been found that the adsorbed formic acid in a monomolecular layer exists as a dissociated or non-dissociated state, according as the adsorbent is alumina or silica. Such difference of state may be noteworthy, in the light of the fact that the catalytic activity of both oxides is similar, i. e., formic acid is dehydrated rather than dehydrogenated, in contrast with the overwhelmingly dehydrogenating activity of metallic powders. It seems, therefore, that there is no direct relation between the adsorbed state and the activated state of decomposition. Concerning this result further research is in progress.

Summary

The state of formic acid adsorbed on silica and alumina has been studied by a combined method of nuclear magnetic resonance and infrared absorption. The adsorbed formic acid in a monomolecular layer has been found not to be dissociated in the case of silica, but to be dissociated in the case of alumina.

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[10] M. Shimizu, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), 78, 21 (1957).

[11] S. Kurosaki, T. Tsuchiya and R. Kawai, ibid., 78, 1806 (1957).

[12] Landolt-Börnstein, "Zahlenwerte und Funktionen", 1, 2. Teil, Springer, Berlin (1951), p. 237.

**** In this table, only the bands in low frequency region were shown. Values in parenthese were obtained by the measurement in which Nujol was not used.