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Decomposition of Formic Acid over Metal Phthalocyanines

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The decomposition of formic acid was studied over two sorts of metal phthalocyanines: Mg- and Fe-phthalocyanines. The rates of the decomposition reactions over Mg-Phc and Fe-Phc were proportional to the pressure of formic acid, and the decomposition proceeded to dehydrogenation as well as to dehydration over these phthalocyanines. The isotope distribution in the hydrogen (H_2, HD, and D_2) produced by the decomposition of HCOOD leads to the conclusion that the hydrogen molecule is mainly formed between the hydrogen atom bonded to the carbon atom and that bonded to the oxygen atom in the formic acid molecule. Formic acid was adsorbed to a considerable extent over Mg-Phc in the temperature range between 70°C and 220°C. The amount of formic acid adsorbed obeyed the Langmuir adsorption isotherm, and the infrared spectra demonstrated the presence of the formate ion $HCOO^-$ on the Mg-Phc. It was also confirmed that Mg-Phc was hydrogenated during the course of the decomposition. The adsorption during the catalytic reaction was also measured. These measurements revealed that the overall rate of the reaction is proportional to the amount of formic acid adsorbed. The mechanism of formic acid decomposition was discussed on the basis of these results.

Catalysis by organometallic compounds in the liquid phase is a topic of great interest in the field of chemistry, and the reactivity of such compounds is in many cases correlated with their electronic properties. In heterogeneous catalysis over metals or metal oxides, the complexity of surface properties, such as the heterogeneity of the surface, frequently brings ambiguity into the elucidation of the reaction mechanism. However, the catalysis by molecular crystals of organometallic compounds proceeds over each of the surface molecules independent of the others, and may be treated as catalysis over each of the surface molecules, as with homogeneous catalysis.

The metal phthalocyanine is a biologically-notable substance as it is similar to heme and chlorophyll in its structure. Over this compound the decomposition of formic acid was studied.[1-3] The reaction is known for its selectivity, as it proceeds to different reaction products, dehydrogenation and dehydration. The selective catalysis over the phthalocyanine molecular crystal is, accordingly, a subject of considerable interest.

The importance of adsorption measurements during the course of the reaction has already been emphasized by one of the present authors.[4] The adsorption on the catalyst surface and the behaviour of the chemisorbed species in its working state is directly associated with the elucidation of the mechanism of the surface catalysis.

In this report, by means of adsorption measurements during the course of the decomposition over the phthalocyanines of magnesium and iron, as well as by means of infrared technique and hydrogen isotope distribution, the mechanism of the catalytic decomposition of formic acid will be studied.

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[1] H. Rosswarm and A. Doiwa, *Naturwissenschaften*, **52**, 159 (1965).

[2] W. Hanke, *ibid.*, **52**, 475 (1965).

[3] W. Hanke, *Z. Anorg. Allgem. Chem.*, **343**, 121 (1966).

[4] K. Tamaru, *Adv. Catalysis* (Academic Press), **15**, 65 (1964).

Experimental

Mg-Phc and Fe-Phc were synthesized according to the Linstead procedures.[5] A magnesium metal film, or iron powder (either 99.9% pure), was boiled with phthalonitrile for 30 hr; the phthalocyanines thus prepared were then carefully purified by washing them with benzene, alcohol, acetone, and water, and by recrystallization in quinoline and by repeated sublimation. The visible and infrared spectra of these phthalocyanines were in reasonable agreement with those reported previously by Linstead[6] and Sidorov[7]. The formic acid was purified by distillation at room temperature, after the removal of the water with anhydrous boric acid. The phthalocyanines of magnesium and iron were evacuated at 250°C and 290°C respectively for 10 hr prior to their use.

The apparatus employed was a closed circulating system with an electromagentic circulating pump. The amount of gases adsorbed on the catalyst surface was calculated from the amount of the reactant introduced into the reaction system and that of the circulating gases. The reactant and products were analyzed by means of gas chromatography: the formic acid, water, and carbon dioxide were analyzed by a dioctyl sebacate (D.O.S.) separatory column, while the carbon monoxide and hydrogen were measured by a silica column at 90°C, employing helium as the carrier gas. The isotopic abundance in hydrogen, H_2, HD, and D_2, was determined by gas chromatography.[8] The infrared cell used in this study was similar to that described previously.[9]

Results and Discussion

I. Adsorption of Formic Acid over Mg-Phc. The adsorption of formic acid over Mg-Phc was studied by a volumetric method at 70, 100, and 130°C, where the decomposition of formic acid scarcely takes place. Due allowance was made for the adsorption of formic acid by the apparatus. The total surface area of the Mg-Phc evaporated film employed was 13.6 m². The adsorption was reversible, and, as shown in Fig. 1, it is approximated by the Langmuir adsorption isotherm; the rate of adsorption was proportional to the formic acid pressure throughout the coverage. The heat of adsorption was estimated from the Clapeyron-Clausius equation to be about 5.5 kcal/mol. The adsorption equilibrium constant was also calculated to be $K=e^{-8.85}e^{5.5\times10^3/RT}$ $mmHg^{-1}$, while the saturated amount of adsorption was 10 m*l* (stp) of monomer formic acid. The number of Mg-Phc molecules in the surface was estimated to be approximately 3.1×10^{11}, asuming that a (001) plane is exposed on the surface, this value corresponds to nearly one-ninth the number of formic acid molecules having saturated adsorption.

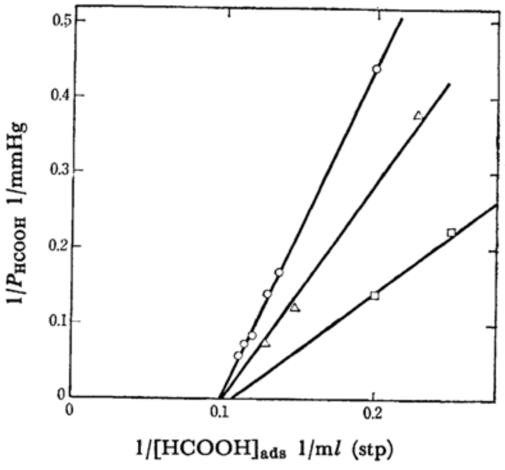

Fig. 1. Dependence of the amount of formic acid adsorbed upon the pressure of formic acid over Mg-Phc.

When water was first adsorbed on Mg-Phc at room temperature, and subsequently formic acid was introduced into the adsorption system, all the preadsorbed water was desorbed, being replaced by the formic acid molecules; this demonstrates that formic acid was adsorbed on the sites where water was adsorbed.

II. Decomposition of Formic Acid. Formic acid was decomposed over Mg-Phc at 200°C. Some typical results are given in Fig. 2, where the amounts of formic acid (m*l*, stp as monomer)

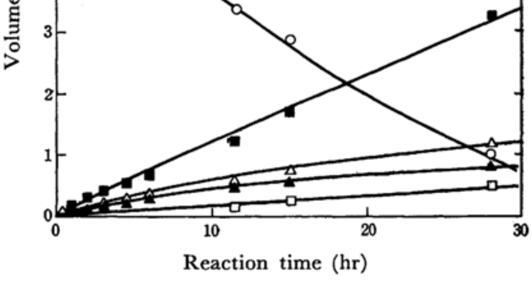

Fig. 2. Decomposition of formic acid over Mg-Phc at 220°C.
○: HCOOH, ■: CO_2, □: H_2, △: H_2O, ▲: CO

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5) R. P. Linstead and A. R. Lowe, *J. Chem. Soc.*, **1934**, 1022.

6) P. A. Barrett, R. P. Linstead, F. G. Rundall and G. A. P. Tuey, *ibid.*, **1940**, 1079.

7) A. N. Sidorov and I. P. Kotlyar, *Optics and Spectroscopy*, **11**, 93 (1961).

8) S. Ohkoshi, Y. Fujita and T. Kwan, This Bulletin, **31**, 771 (1958).

9) Y. Noto, K. Fukuda, T. Onishi and K. Tamaru, *Trans. Faraday Soc.*, **63**, 2300 (1967).

and of the reaction products (m*l*, stp) are plotted against the reaction time (hr). Trace amounts of HCHO, CH_3OH, and $HCOOCH_3$ were also detected.[*1] It should be noted here that the amount of hydrogen produced was much less than that of carbon dioxide.

The results obtained over Fe-Phc, where the total surface area is 1.6 m², are shown in Fig. 3. In this case as much hydrogen as carbon dioxide was evolved unlike the case of Mg-Phc. The ratios of dehydration to dehydrogenation were 1 : 5 at 200°C and 1 : 3 at 279°C.

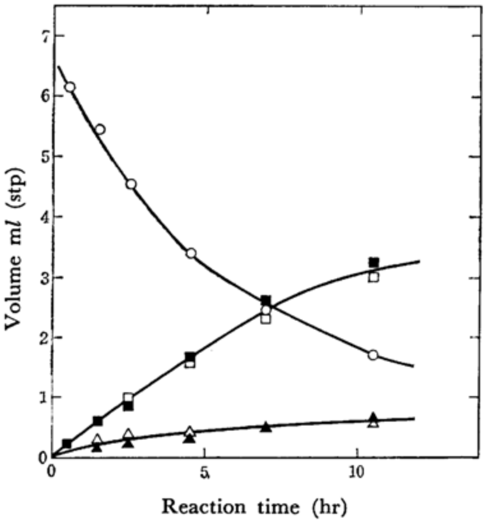


Fig. 3. Decomposition of formic acid over Fe-Phc at 232°C.

○: HCOOH, ■: CO_2, □: H_2, △: H_2O, ▲: CO

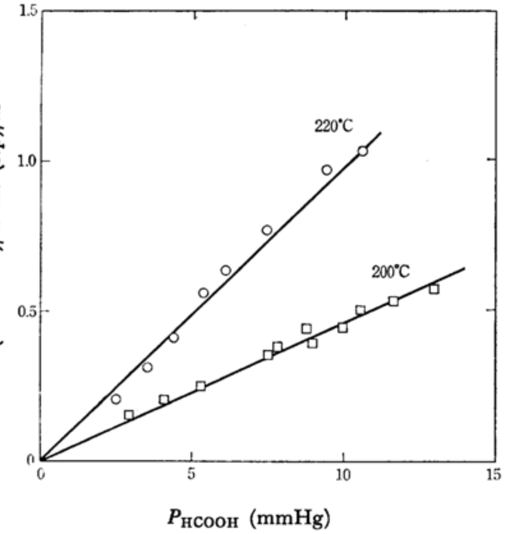


Fig. 4. Dependence of the rate of the decomposition of formic acid upon the partial pressure of formic acid over Mg-Phc.

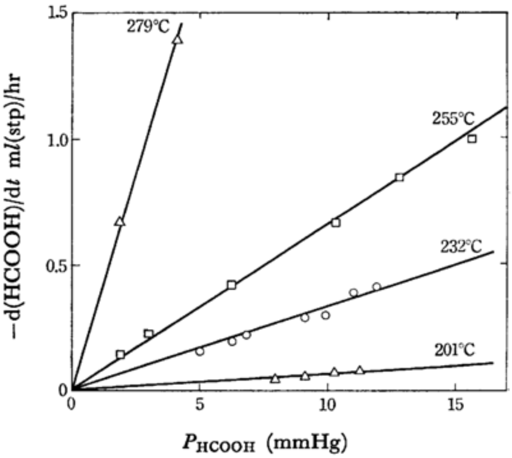


Fig. 5. Dependence of the rate of the decomposition of formic acid upon the partial pressure of formic acid over Fe-Phc.

The rates of formic acid decomposition over Mg-Phc and Fe-Phc were proportional to the pressure of formic acid, as is shown in Figs. 4 and 5. The temperature dependence of the decomposition rate gave the activation energies for the decomposition as 17 kcal/mol for Mg-Phc and 26.1 kcal/mol for Fe-Phc. The frequency factors were calculated to be $5.5\times10^2(\mathrm{m})^{-2}(\mathrm{sec})^{-1}$ for Mg-Phc and $1.1\times10^7(\mathrm{m})^{-2}(\mathrm{sec})^{-1}$ for Fe-Phc.

The adsorption during the decomposition on Mg-Phc was estimated from Fig. 2; it is given in Fig. 6. The composition of the adsorbate was approximately equal to that of formic acid in the first stage of the reaction; later it had a composition richer in hydrogen. The amount of formic acid in the first stage of the reaction was in conformity with the amount estimated by the extrapolation of the adsorption equilibrium up to the

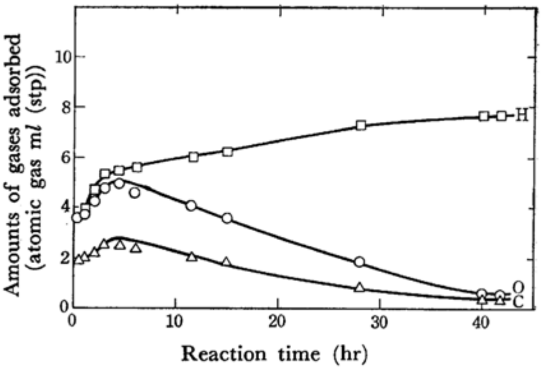


Fig. 6. The adsorption during the course of the decomposition of formic acid over Mg-Phc at 220°C.

[*1] CH_3OH and $HCOOCH_3$ were clearly found by infrared spectra when formic acid was decomposed at 150°C.

reaction temperature. Water, hydrogen, carbon monoxide, and carbon dioxide were separately introduced over the phthalocyanine; it was confirmed that these gases were not adsorbed in the temperature range studied. These results suggest that Mg-Phc is hydrogenated during the course of the formic acid decomposition.

From the results given in Fig. 6, the amount of formic acid adsorbed was plotted against the rate of the decomposition; this plot is given in Fig. 7, where a linear relation was obtained under similar reaction conditions. The adsorption over Fe-Phc, the total surface area of which was 17 m², was much less than that over Mg-Phc, and Fe-Phc was not hydrogenated during the course of the decomposition.

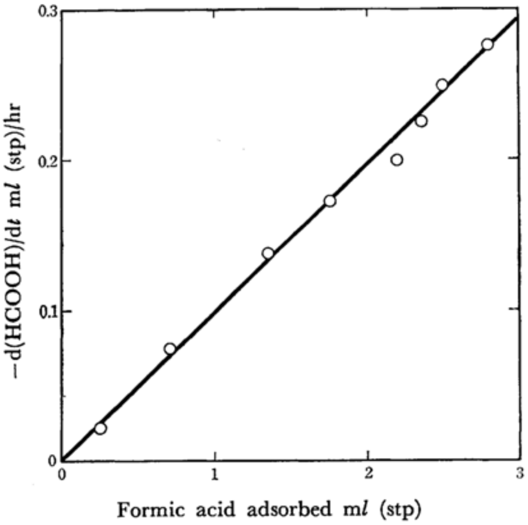


Fig. 7. Dependence of the rate of the decomposition of formic acid upon the amount of formic acid adsorbed over Mg-Phc at 220°C.

When the monodeuterated formic acid, HCOOD, was introduced onto the hydrogenated Mg-Phc, which had previously been evacuated for 10 hr at 250°C, an exchange reaction took place between the deuterium in the HCOOD and the hydrogen in the hydrogenated Mg-Phc, and exchange equilibrium being reached at 100°C. Then the ambient HCOOD was replaced by HCOOH; HCOOD was consequently formed. Accordingly, during the reaction, the isotopic mixing takes place between the hydrogen in water, that in the OH group of formic acid, and that added to the phthalocyanine. The hydrogen in a fresh Mg-Phc, or Fe-Phc, on the other hand, did not participate in the exchange reaction, and no hydrogen exchange with HCOOD could be detected.

When HCOOD was decomposed over a fresh Mg-Phc at 220°C, the ratio of hydrogen to deuterium in the hydrogen gas produced was the same as in the case of HCOOD, though a part of the hydrogen was fixed by the phthalocyanine. The isotopic abundance in the hydrogen produced is given in Table 1.

TABLE 1

Catalyst		Observed %	Equilibrium value %
Mg-Phc*	H_2	13	32
	HD	84	46
	D_2	3	22
Fe-Phc**	H_2	18	29
	HD	79	48
	D_2	3	23

* The D content in HCOOD was 90%.
** The D content in HCOOD was 95%.

Hydrogen was mostly HD, while D_2 corresponded to 13.6% of the equilibrium value of the isotopic exchange.

When HCOOD was similarly decomposed over Fe-Phc at 250°C, a considerable amount of HD was produced and the D_2 corresponded to 12.9% of the exchange equilibrium. It may, accordingly, be concluded that the majority of the hydrogen was produced between the hydrogen bonded to carbon and that bonded to oxygen. The H_2-D_2 exchange reaction did not proceed over Mg-Phc or Fe-Phc under the conditions of formic acid decomposition.

Formic acid was repeatedly introduced over Mg-Phc in order to continue the decomposition for more than 20 days at 220°C. The colour of the Mg-Phc film thereupon changed from violet to blue. When formic acid was decomposed over the catalyst thus treated, the amount of hydrogen produced was the same as that of carbon dioxide; this seemingly suggests the saturation of the hydrogenation. The selectivity or the ratio of CO_2 to CO in the reaction products was not changed.

The infrared spectra, in the region from 4000 to 700 cm⁻¹, of the evaporated Mg-Phc film on a NaCl plate are shown in Fig. 8(a). The spectra were those of the α-form of Mg-Phc. When the Mg-Phc was evacuated for two hours at 200°C, its infrared spectra were changed to the β-form, as is shown in Fig. 8(b). The spectra changed markedly when the β-form of Mg-Phc was treated with 2 cmHg formic acid for a few hours at 100°C, as is shown in Fig. 8(c). The change in the spectra was almost the same as that when CH_3COOH was adsorbed on the α-form of Mg-Phc at room temperature.[10] Most of the change may be interpreted as being due to the α-β transformation. In addition to this change, the spectra of the formate ion, such as 1610 and 1375 cm^{-1}, were observed; this indicates that formic acid was adsorbed on the Mg-Phc, dissociating to a formate ion and a proton. When

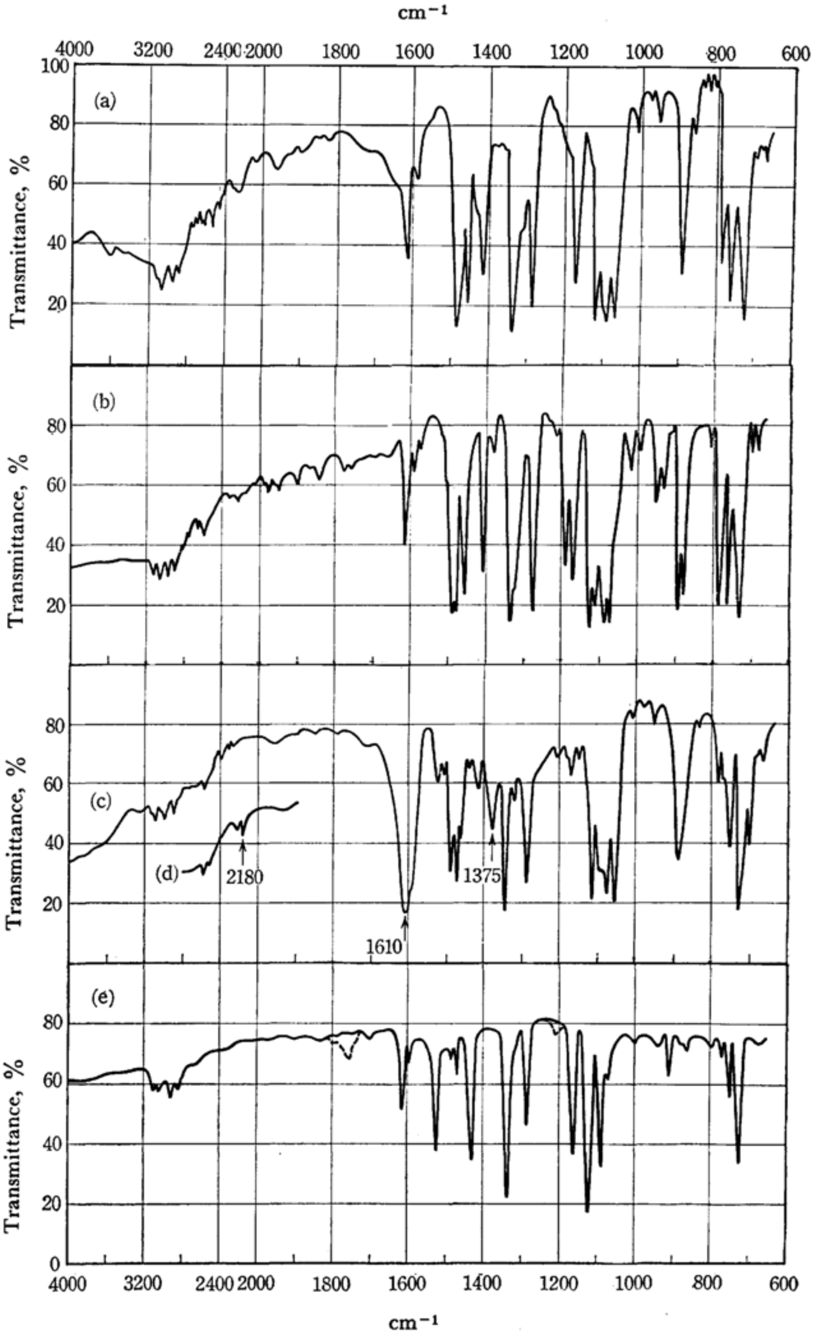


Fig. 8. (a) Infrared spectra of evaporated Mg-Phc film.
(b) Infrared spectra of the Mg-Phc film treated at 200°C.
(c) Infrared spectra of the Mg-Phc where formic acid is adsorbed at 70°C.
(d) Infrared spectra of adsorbed DCOOD on Mg-Phc during the course of the decomposition at 150°C.
(e) Infrared spectra of Fe-Phc (——) and after the exposure to HCOOH vapour at room temperature (- - -).

the Mg-Phc which adsorbed formic acid was evacuated for two hours at 200°C, the spectra of the formate ion disappeared and the structure of the phthalocyanine returned to the β-form.

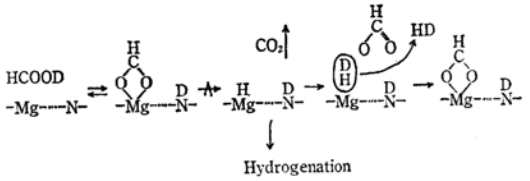
The infrared spectra were also studied during the decomposition of DCOOD over Mg-Phc for ten hours at 150°C, as is shown in Fig. 8(d); a new weak band at about 2180 cm^{-1} was observed, a band which became stronger with the progress of the decomposition. The band at $2180\ \text{cm}^{-1}$ is close to that of the ND^+ stretching vibration, which appears when DCl is adsorbed on Mg-Phc, deuterium being added to the peripheral nitrogen of Mg-Phc.[10] This band did not disappear upon evacuation. After evacuation, HCOOH was introduced into the reaction system and the band at $2180\ \text{cm}^{-1}$ rapidly disappeared.

When Fe-Phc which had been evacuated for two hours at 220°C was exposed to formic acid for a few hours in the temperature range between room temperature and 100°C, neither any formate ions nor any changes in its crystal structure were detected, except for the weak peaks resulting from physically adsorbed formic acid.

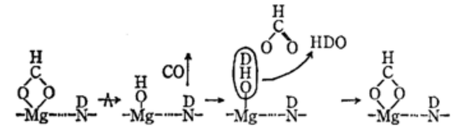
From these results, it was concluded that the hydrogenation takes place at the nitrogen of Mg-Phc and that the hydrogen thus fixed can exchange with the proton in the formic acid molecules. Formic acid is adsorbed over Mg-Phc, dissociating to a formate ion and a proton, as is demonstrated in the infrared spectra. The adsorption quickly reaches an adsorption equilibrium, and the amount of formic acid adsorbed in the first stage of the reaction is in conformity with the amount calculated from the adsorption equilibrium.

The linear relation between the adsorption and the overall rate of the decomposition excludes the possibility of the mechanism of the reaction taking place between the adsorbed species and the acid molecule in the ambient gas. It indicates that the reaction intermediate for the decomposition over Mg-Phc is the adsorbed species, or the surface formate ion, and that the reaction takes place *via* the unimolecular decomposition of the formate ion in a manner similar as that over zinc oxide.[11]

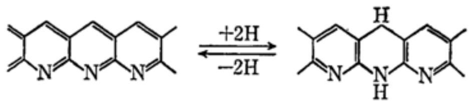
The amount of hydrogen evolved was much less than that of carbon dioxide in the initial stage of the decomposition, and Mg-Phc is hydrogenated during the course of the decomposition. The hydrogen thus added to Mg-Phc takes part in the exchange reaction with the hydrogen of the OH group in the formic acid and water molecules. Accordingly, when HCOOD was decomposed over Mg-Phc the hydrogenation of Mg-Phc proceeds to the extent of the reaction; this results in the quick mixing of hydrogen isotopes in the hydrogen bonded to oxygen in the acid and water. The hydrogen-isotope mixing should not be marked in the initial stage of the reaction, where the extent of hydrogenation, and also the amount of water produced, are little. As the rate of hydrogen evolution was much slower than that of carbon dioxide, it took some time to collect enough hydrogen sample for the isotopic analysis; this delay inevitably results in some isotopic mixing. If we take this mixing into consideration, the results given in Table 1 indicate that dehydrogenation overwhelmingly takes place, forming hydrogen from the hydrogen in OH and from that of the CH in the formic acid molecule, as follows, in a manner similar to that with ZnO:[11]



The selectivity of the decomposition, on the other hand, was independent of the extent of hydrogenation; this suggests that different reaction intermediates can be excluded for the dehydrogenation and dehydration for instance, the hydrogen in the phthalocyanine molecule added from the acid molecule. As the dehydration also proceeds in proportion to the amount of adsorption, the following mechanism may be considered for the dehydration:



It has been reported that some organic polymer catalysts are also hydrogenated.[12] For example, polycyanoacetylene was hydrogenated during the course of the dehydrogenation of alcohol or cyclohexene, as follows:



The uptake of hydrogen by the organic polymers is interesting in connection with the behaviour of Mg-Phc.

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10) A. N. Sidorov and A. N. Terenin, *Optics and Spectroscopy*, **11**, 175 (1961).

11) Y. Noto, K. Fukuda, T. Onishi and K. Tamaru, *Trans. Faraday Soc.*, **63**, 3081 (1967).

12) J. Manassen and J. Wallch, *J. Am. Chem. Soc.*, **87**, 2671 (1965).