SHORT COMMUNICATIONS

The Dehydrogenation of Formic Acid over Zinc Oxide*[1]

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The dehydration of formic acid has been studied previously by the authors over alumina and silica-gel.[1] It was accordingly concluded that the decomposition takes place *via* the surface proton which was supplied from formic acid, while the formate ion is not the reaction intermediate. On the surface of silica-gel on the other hand, the dehydration reaction proceeds *via* the original surface OH group.

The dehydrogenation decomposition of formic acid over zinc oxide was studied by several investigators and a variety of mechanisms have been proposed. In this communication the amounts and the infrared spectra of the adsorbed species and their dynamic behaviour were measured during the course of the decomposition. When formic acid was brought into contact with zinc oxide, a neutralization reaction to form bulk metal formate and water took place, and a large quantity of water appeared in the gas phase as the uptake of formic acid proceeded. From the infrared spectra, it was confirmed that all the adsorbed species were chemisorbed formate ion.[2] When DCOOD was introduced to zinc oxide pretreated with HCOOH to form $(HCOO)_2Zn$, the surface monolayer of formate ions only exchanged with the gaseous formic acid. From the isotopic abundance in the hydrogen produced, it was revealed that the formate ion in the surface layers only participates in the decomposition.

The decomposition in the stationary state proceeded almost to dehydrogenation in the temperature range between 145 and 220°C. As is shown in Fig. 1, the rate of the decomposition was not relevant to the pressure of formic acid, being a zero-order reaction, and the ratio of the gas produced, CO_2/H_2, was unity provided formic acid was present in the gas phase. However, if formic acid was trapped out of the ambient gas, the evolution of hydrogen stopped correspondingly, while the rate of evolution of carbon dioxide stayed constant. When the formic acid was introduced again in the gas phase, hydrogen evolved rapidly and finally the amount of carbon dioxide and hydrogen became the same, and the decomposition was continued as a zero-order again.

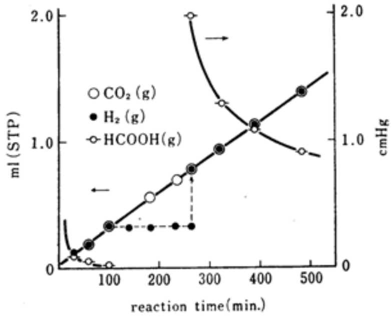
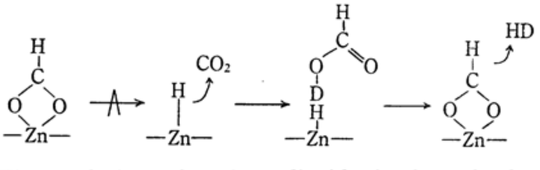


Fig. 1. Decomposition of formic acid on ZnO at 154°C.

It was revealed that the decomposition proceeded with the same reaction order and with the same activity over zinc formate as on zinc oxide. When HCOOD was decomposed on $(HCOO)_2Zn$, the hydrogen produced was practically all HD.

On the basis of these results the mechanism of the dehydrogenation of formic acid on zinc oxide is as follows.



The evolution of carbon dioxide is through the decomposition of formate ion on the surface, and hydrogen atom remains on the surface in the absence of formic acid. Gaseous hydrogen appears when formic acid molecules attack the surface hydrogen atom, which results in the formate ion on the surface in turn. This is also supported by the fact that only HD appeared when HCOOD was decomposed on $(HCOO)_2Zn$.[3]

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*[1] Presented at the 20th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1967.

1) Y. Noto, K. Fukuda, T. Onishi and K. Tamaru, accepted for publication in *Trans. Faraday Soc.* K. Fukuda, Y. Noto, T. Onishi and K. Tamaru, accepted for publication in *Trans. Faraday Soc.*

2) The presence of formate ion was independently observed by T. Kondo, T. Ogawa and K. Hirota, (20th Ann. Meeting of Chem. Soc. Japan, April, 1967, Tokyo)

3) Y. Noto, K. Fukuda, T. Onishi and K. Tamaru, accepted for publication in *Trans. Faraday Soc.*