BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 1760—1761 (1969)

# The Mössbauer Spectrum of Iron Adsorbed on an Anion Exchange Resin

Yoshimasa TAKASHIMA, Yonezo MAEDA and Shunji UMEMOTO

*Department of Chemistry, Faculty of Science, Kyushu University, Fukuoka*

(Received October 2, 1968)

It is well known that iron(III) is strongly taken up on an anion exchange resin from relatively concentrated hydrochloric acid solutions. This fact can be interpreted on the basis of the results of chemical analysis, as indicating formation of negatively-charged complex ions, $FeCl_4^-$. Because of the opacity of resins, most spectroscopic techniques are not applicable to the direct investigation of chemical species sorbed on ion exchange resins. However, Mössbauer spectroscopy can be applied to such a study because penetrating $\gamma$ rays are used in this technique. Several studies along this line have already been reported,[2,3] and interesting results have been obtained concerning the nature of individual species sorbed on ion exchangers.

The present paper is concerned with Mössbauer spectroscopic study of iron(III) sorbed on an anion exchange resin; the study was undertaken in order to confirm the symmetry and coordination of ligands surrounding the iron atom.

### Experimental

**Materials.** The resin sample was prepared by passing a solution containing 27 g of $FeCl_3 \cdot 6H_2O$ in 100 m*l* of 7M hydrochloric acid through a column of Dowex 1-X4 (100—200 mesh); the excess solution was removed by washing the sample with 7M hydrochloric acid. Two types of samples, wet and dry, were used for the measurements. The dry sample was prepared by drying the resin obtained above in a vacuum dessiccator.

The selected reference samples, $KFeCl_4$, $NH_4FeCl_4$, *etc.*, were prepared according to the procedure used by Friedman and Taube.[4]

**Mössbauer Spectrometer.**[5] A multichannel pulse-height analyser coupled with an instantaneous velocity measurement of the $\gamma$ ray source was used. The source of radiation was $^{57}$Co diffused onto metallic copper. The spectrometer was calibrated by sodium nitroprusside, and the isomer shift was expressed in mm/sec relative to the center of the nitroprusside spectrum. The measurements were performed both at room temperature and at the temperature of liquid nitrogen.

### Results and Discussion

No discernible Mössbauer effect was observed for the resin samples at room temperature, but one was observed at the temperature of liquid nitrogen. Unlike the resin samples, all the reference samples showed a measurable effect, even at room temperature. All of the spectra obtained showed a fairly sharp single absorption, which is responsible for the symmetrical charge distribution around the iron atom. Table 1 summarizes the results obtained by the Mössbauer measurements of the resins and the other reference samples. The errors involved in Table 1 showing the estimation of the isomer shifts were about ±0.02 mm/sec; the variation in the isomer shift, depending on the temperature, was estimated to be small (probably less than 0.05 mm/sec).

TABLE 1. ISOMER SHIFT

| Sample | Temperature | Isomer shift* (mm/sec) | Coordination |
|---|---|---|---|
| Wet resins | liq.-$N_2$ temp. | 0.57 | |
| Dry resins | liq.-$N_2$ temp. | 0.54 | |
| $KFeCl_4$ | liq.-$N_2$ temp. | 0.54 | tetrahedral, $4Cl^-$ |
| $KFeCl_4$ | room temp. | 0.54 | tetrahedral, $4Cl^-$ |
| $NH_4FeCl_4$ | room temp. | 0.50 | tetrahedral, $4Cl^-$ |
| $FeCl_3$ | liq.-$N_2$ temp. | 0.73 | octahedral, $6Cl^-$ |
| $FeCl_3$ | room temp. | 0.70 | octahedral, $6Cl^-$ |
| $FeCl_3 \cdot 6H_2O$ | room temp. | 1.12<br>0.12 | octahedral |

* Relative to the center of sodium nitroprusside.

Between the values of the isomer shift for typical tetrahedral and octahedral compounds, a remarkable difference was found. Since the isomer shift reflects the degree of covalency, we may conclude from this observation that the tetrahedral compounds have more covalent bonds than the octahedral compounds.

The strong similarities between the isomer shift of the resin samples and that of the tetrahedral

---

1) G. E. Moore and K. A. Kraus, *J. Am. Chem. Soc.*, **72**, 5792 (1950).

2) S. Y. Wang, A. H. Lu and P. G. Tseng, *Chinese J. Phys.*, **2**, 50 (1964).

3) J. L. Mackey and R. L. Collins, *J. Inorg. Nucl. Chem.*, **29**, 655 (1967).

4) H. L. Friedman and H. Taube, *J. Am. Chem. Soc.*, **72**, 2236 (1950).

5) Y. Takashima and S. Ohashi, Presented at the 20th Annual Meeting of the Chemical Society of Japan, Tokyo, March, 1967; Abstract II, p. 212.

compounds suggest that the iron sorbed on the anion exchange resin is in a tetrahedral environment.

It is also noticed that there is very little difference in the isomer shift between wet and dry resin samples.

This indicates that the water molecules play only a minor role in the coordination sphere of the iron sorbed on the resins.

It may be reasoned from the data on $FeCl_3$ and $FeCl_3 \cdot 6H_2O$ that the isomer shift distinctly increases as chloride ligands bound to central iron(III) ion are replaced by the less polarizable water ligands. In view of the above results, it may be concluded that the iron(III) sorbed on an anion exchanger under these experimental conditions in the undistorted tetrahedral coordination sphere which arises from chloride ligands. There are two peaks in the absorption of $FeCl_3 \cdot 6H_2O$. However, we do not yet know their exact origins.6)

---

6) W. Kerler, *Z. Physik*, **167**, 194 (1962); H. Bernas and M. Langevin, *J. Phys.*, **24**, 1034 (1963).