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Infrared Absorption Spectra and Oxidation of Iron(II) Hydroxide and Green Rust I

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Transformations on oxidation of hydroxide and basic salts of iron (II) have been investigated by means of X-ray and electron diffraction.[1-4] Infrared spectroscopy was applied for the observation of hydroxide and basic chloride of iron (II) in aqueous solutions. The infrared spectra of iron (II) hydroxide and Green Rust I, an oxidation intermediate, were obtained for the first time. No absorption band attributable to other intermediate compounds appeared in the course of oxidation.

Iron (II) hydroxide and basic chloride were prepared by adding adequate quantities of potassium hydroxide to the oxygen free aqueous solutions of iron (II) chloride (0.39 mol/*l*). The precipitates formed were separated from solutions by centrifugation. The infrared absorptions due to the water remaining in the precipitates were compensated by means of a reference cell containing a thin film of water. The oxidation of the precipitates in solutions was carried out at room temperature by introducing air at a constant rate of 1 *l*/min.

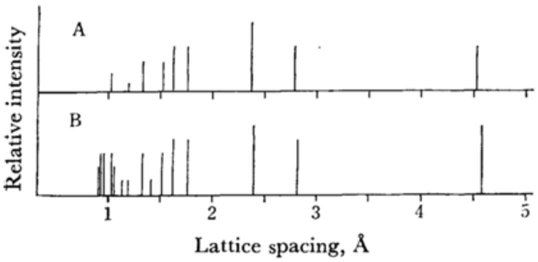

Fig. 1. X-Ray diffraction diagram of iron (II) hydroxide
A: present work B: Bernal *et al.*[1]

The precipitate obtained from basic solution (pH; 12.5—13.5), which was identified as iron (II) hydroxide by X-ray diffraction (Fig. 1), has two sharp absorption bands at 3630 and 480 cm^{-1}. The intensities of these two bands decreased with the progress of oxidation, and the absorption bands characteristic of α-FeOOH appeared. After oxidation for 30 hr, the absorption bands of iron (II) hydroxide disappeared completely, and only the bands due to α-FeOOH could be observed. Bernal *et al.* suggested an oxidation intermediate of Fe-(O,OH).[1] However, no band attributable to such an intermediate compound could be detected.

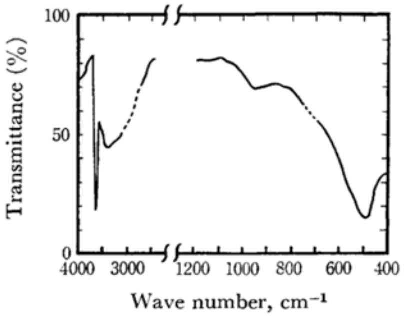

Fig. 2. Infrared absorption spectrum of iron (II) hydroxide obtained with Nujol mulling technique

Iron (II) hydroxide separated from solution was repeatedly washed with oxygen free ethanol and with petroleum ether so as to minimize the absorptions of water. The infrared spectrum of iron (II) hydroxide thus obtained is shown in Fig. 2. The high wavenumber and sharpness of the absorption band arising from O–H stretching vibration indicate that the OH group in iron (II) hydroxide is almost free from hydrogen bonding. The band at 480 cm^{-1} may be assigned to the translational mode of OH group by analogy with the spectrum of metal hydroxide having the same CdI_2 type structure as iron (II) hydroxide.[5]

The X-ray diffraction pattern showed that the precipitate formed in a slightly acidic solution (pH; 6.0—6.5) consisted of β-$Fe_2(OH)_3Cl$ and Green Rust I. The infrared absorption bands of the precipitate were located at 3540, 800, 670 and 470 cm^{-1}. While the relative intensity of the absorption band at 470 cm^{-1} decreased monotoni-

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[1] J. D. Bernal, D. R. Dasgupta and A. L. Mackay, *Clay Minerals Bull.*, **4**, 15 (1959).

[2] T. Takada, T. Akita and M. Kiyama, Paper presented at the 21st Annual Meeting of the Chemical Society of Japan, April 1, 1968, and preceding papers.

[3] H. Yoshioka, *J. Phys. Soc. Japan*, **4**, 270 (1949).

[4] H. R. Oswald and W. Feitknecht, *Helv. Chim. Acta*, **44**, 847 (1961); *ibid.*, **47**, 272 (1964).

[5] O. Oehler and Hs. H. Günthard, *J. Chem. Phys.*, **48**, 2036 (1968).

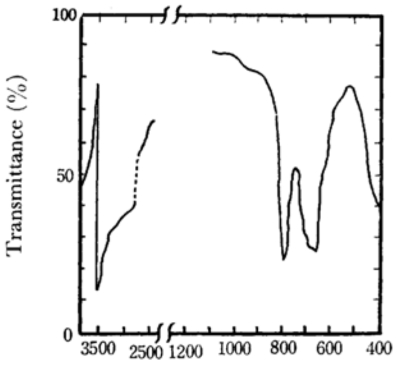

Fig. 3. Infrared absorption spectrum of Green Rust I (Nujol mull)

cally on oxidation, the bands at 3540, 800 and 670 cm^{-1} increased at first and then decreased in intensity. Since the increase of relative quantity of Green Rust I in the precipitate with oxidation was found at an early stage of oxidation by the X-ray diffraction measurement, it is likely that the latter three bands arise from the vibration of Green Rust I. The precipitate formed in neutral or slightly basic solution (pH; 7.0—8.0), was a mixture of iron (II) hydroxide and Green Rust I and was transformed to Fe_3O_4 by oxidation. It had absorption bands at 800 and 670 cm^{-1} besides the bands of $Fe(OH)_2$. This fact agrees with the assignment of the above mentioned bands to Green Rust I.

The infrared absorption spectrum of the precipitate formed in the slightly acidic solution and washed with ethanol and petroleum ether is shown in Fig. 3. The broad band at 470 cm^{-1} belonging probably to β-$Fe_2(OH)_3Cl$ disappears in the spectrum. It seems that β-$Fe_2(OH)_3Cl$ is not stable and decomposed during the course of washing with organic solvents, and thus Fig. 3 shows the spectrum of Green Rust I.

Bernal *et al.* claimed that Green Rust I might be transformed first to Green Rust II and then to γ-FeOOH.[1)] Since all the absorption bands appearing on the oxidation of Green Rust I belonged to γ-FeOOH, it can be deduced that Green Rust I was not transformed as a whole to Green Rust II in the present investigation.