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IR SPECTRA OF THE REACTION PRODUCTS BETWEEN IRON VAPOR AND NITRIC OXIDE: A MODEL FOR THE CHEMISORPTION OF NITRIC OXIDE

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Based on the IR spectroscopic study of the reaction products between iron vapor and nitric oxide, which can be regarded as a model of chemisorbed species, the IR absorption bands of nitric oxide adsorbed on iron at 1800 and 1720 cm^{-1} are attributed to adsorbed species on oxidized and metallic iron, respectively.

Recently the matrix isolation technique has been developed in metal atom chemistry$^{1)}$ where high reactivity of atomic metals is utilized to prepare various reaction products with various gases.$^{2)}$ The products of the reaction can be trapped onto a cold plate, and examined by spectroscopic techniques. By this method one can study the IR spectra of metal complex products over whole wave number range of interest. IR studies of the chemisorbed species on supported metals can only be applicable to a limitted range of spectra because of wide-ranged background absorption. The complexes obtained in such a way are supposed to be a model for chemisorption complexes or intermediates in the reaction occurring on a metal surface.

In this letter, IR spectra of the reaction products between iron vapor and nitric oxide are studied. Making use of the above mentioned advantage of this approach, the IR spectra of NO adsorbed on metallic iron and oxidized iron will be reported.

The apparatus is consisted of a metal evaporation chamber and a low temperature IR cell, which will be described elsewhere. Iron was vaporized by heating iron metal in an alumina-coated tungsten crucible resistively and reacted with gases admitted through an inlet-tube. The reaction products were deposited on a CsBr window which had been cooled down by liquid nitrogen. During the reaction non-trapped gas was pumped out and the pressure in the apparatus was maintained below 10^{-3} Torr.

Figure 1 shows the IR spectra of the products obtained by the reaction of iron vapor with nitric oxide taken at various temperatures. Strong bands at 1800 cm^{-1} and 1720 cm^{-1} are due to the N-O stretching vibration of NO coordinated to iron. A weak band at 2240 cm^{-1} is attributable to solid N_2O resulted from partial decomposition of NO during the reaction, since it was first removed by warming-up the specimen evolving N_2O gas.

The relative intensity of 1800 cm^{-1} band to 1720 cm^{-1} band increased by the warm-up experiment. It further increased slowly by standing at room temperature. On the other hand, the intensity ratio was scarcely affected by cooling down to 77 K again or by further deposition of iron vapor on the sample which gave the spectrum C in fig. 1. These facts show that the two bands are attributable to the different NO species: the one which gives the band at 1800 cm^{-1} is more stable than that at 1720 cm^{-1}. The IR spectra of NO adsorbed on metals show usually a few bands in the N-O stretching region indicating the existence of various adsorbed states.3) It might be due to the different adsorbed states of NO on a simple substrate surface or alternatively to the different substrate states. The latter view can be important for the NO adsorption on base metals which are highly reactive to NO and are easily oxidized to their oxides. It should be noted that in low wave number region, a

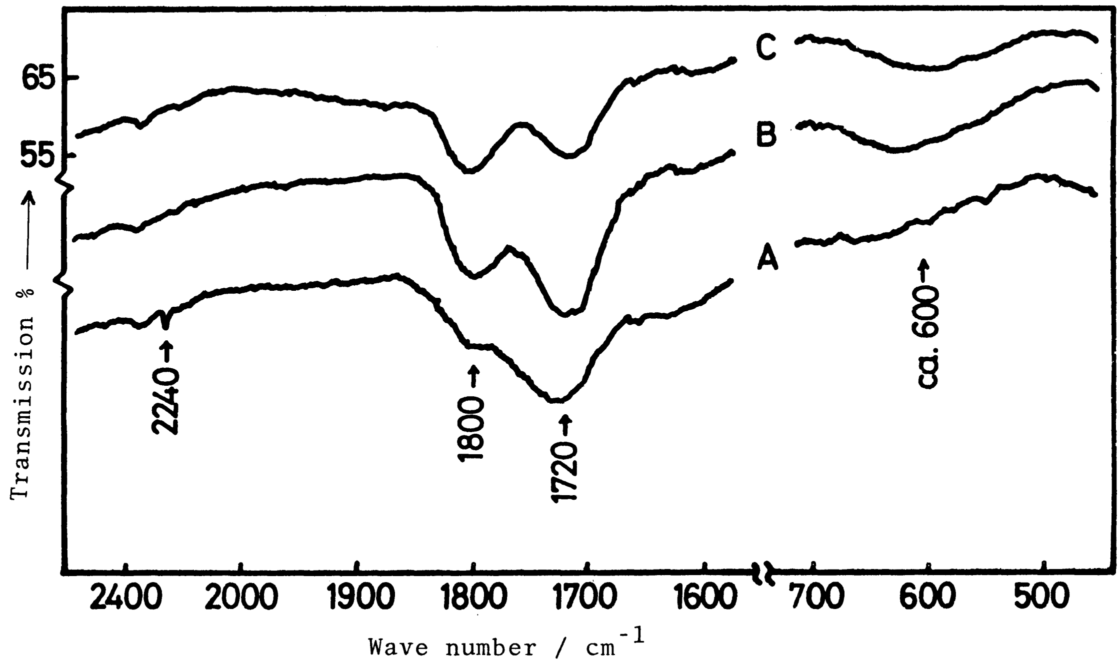

Fig. 1. IR spectra of the products obtained by Fe(vap.) + NO.
A: Fresh sample, recorded at 77 K, B: after warming-up slowly to 293 K,
C: after warming-up to ca. 320 K. Spectrum B and C were recorded at 293 K.

broad band centered at 600 cm^{-1} becomes prominent at room temperature as shown in spectrum B in fig. 1. Blyholder and Allen reported that a broad band at 600 cm^{-1} appeared when NO was admitted to iron metal,4) and also reported surface oxide of iron to give a broad band at 600 cm^{-1}.5) Accordingly the band at 600 cm^{-1} can be due to iron oxide which is formed by the decomposition of NO adsorbed on iron metal during the warming-up to 293 K. Comparing the spectrum A with B in fig. 1, the increase in the intensity of the 1800 cm^{-1} band accompanies with the growth of the 600 cm^{-1} band. Therefore it is suggested that the 1800 cm^{-1} band is attributable to the adsorbed NO on oxidized iron. On the other hand, the band at 1720 cm^{-1} can be due to NO bound to metallic iron.

The assignment finds additional evidences in the following results. Figure 2 shows the IR spectra of the products obtained by the reaction of Fe(vap.) + NO, and with H_2 or CO in the reactant gas. Comparing the spectrum A with B and C, it is obvious that the amount of the species which gives the band at 1800 cm^{-1} is less when H_2 or CO is included in the reactant gas. Correspondingly, the band due to iron oxide was absent in a low wave number range in each case. H_2 or CO reacts with oxygen left on iron by NO decomposition, as is confirmed from the fact that H_2O or CO_2 was detected in the IR spectra of the deposit of the reaction products at 77 K. H_2 or CO in the reactant gas, thus, prevents the formation of oxidized iron, reducing the intensity of the band due to NO adsorbed on oxidized iron. Blyholder and Allen have previously reported that NO adsorbed on iron in a oil matrix shows three bands at 1810, 1720, and 600 cm^{-1}.4) These bands located at almost the same positions as observed in our case, but different in intensity. They considered that these two bands at 1810 and 1720 cm^{-1} are due to the adsorbed NO on low coordination number

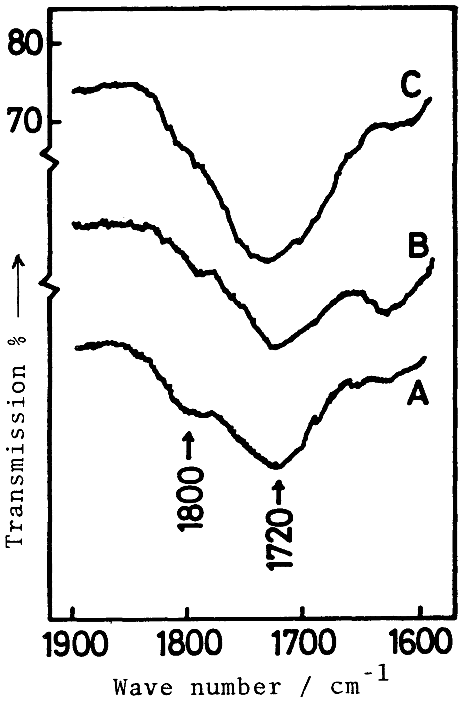

Fig. 2. IR spectra of fresh samples obtained by the reaction of Fe(vap.) and NO in different composition gas. Reactant gas, A: NO only, B: NO + H_2(1:1), C: NO + CO(2:1). All spectra were recorded at 77 K. A band at 1620 cm^{-1} are due to solid H_2O in contamination and reaction products.

sites(edge, dislocation etc.), and high coordination number plane face sites, respectively, on the basis of the molecular orbital consideration. However, as mentioned above, the present assignment seems more probable. The fact that the 1810 cm^{-1} band is stronger than the 1720 cm^{-1} band in their spectra is associated with a rather strong band at 600 cm^{-1}, which means that the oxidation of iron proceeded in this case further than in our case.

It is accordingly demonstrated that by the present approach it is possible to study the IR absorption spectra of "chemisorption complexes" in the whole wave number range without any interference of support prior to the fast secondery reaction to take place, which leads us the first umambiguous assignment of the IR spectra of NO chemisorbed on iron.

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