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# Displacement of Carbon Monoxide from Iron Films by Mercaptans

Many infrared studies (*1*, *2*) have been concerned with spectra of CO chemisorbed on various transition metals. A few (*3–6*) have used iron as an adsorbent, and of these only one deals (*6*) with iron films. This is due, in part, to the fact that it is difficult to obtain a spectrum of CO chemisorbed on supported iron. The spectrum of CO chemisorbed on iron exhibits a single band near 1950 $cm^{-1}$ and has been attributed to CO bonded to the surface in a linear structure, $Fe–C{\equiv}O$ (*3*).

Spectra for the displacement of CO from nickel films are illustrated in another paper (*7*). In that work it was found that the band due to linearly bonded CO did not shift frequency as it was displaced, while the low wave number band did exhibit a shift in position. This was explained in terms of a variety of "bridge bonded" type species having differing Ni–C bond strengths. Because CO on iron has only one absorption in the infrared spectrum near 2000 $cm^{-1}$, and since this bond is somewhat asymmetric as is the low wave number band on Ni, we decided to see what effect using a mercaptan as a displacing molecule would have on the resulting spectra. The questions we sought to answer were (i) will the CO be more easily displaced from iron than nickel, and (ii) will the results more nearly duplicate those observed for the high or low wave number band for CO on nickel.

Iron films were prepared by evaporation from a heated tungsten filament following a procedure described by Blyholder (*8*). The specific cell design has been presented elsewhere (*9*). Films prepared in this manner are not to be considered clean. However, materials which may be adsorbed on contact with the oil are apparently weakly held to the surface since many gases have been found to readily chemisorb on the metal.

All spectra were recorded using a Beckman IR-10 spectrometer equipped with an external recorder. The iron and tungsten were obtained in the form of high purity wire from A. D. Mackay, Inc. The CO was supplied by the Air Reduction Co. as CP grade. The $H_2$ and He were supplied by Big 3 Industries. The $H_2$ and He were purified by passing over hot copper turnings at 420°, then through two traps cooled with liquid nitrogen. The second trap contained activated charcoal. The CO was purified by passage through a charcoal trap immersed in liquid nitrogen. The mercaptans were supplied by Eastman Organic Chemicals (1-propanethiol) and Aldrich Chemical Co. These were subject to several freeze–thaw cycles with pumping and stored in glass vessels on the vacuum system.

After preparing the film a background spectrum was recorded. The cell was subsequently returned to the vacuum system and carbon monoxide at approximately 3 Torr (1 Torr = 133.3 $Nm^{-2}$) added to the cell. After approximately 30 min the gas phase CO was removed by pumping to at least $10^{-4}$ Torr and another spectrum recorded. After recording this spectrum a small amount of mercaptan (about $10^{-3}$ Torr) was admitted to the cell. Other experiments indicated no changes in the spectra occurred after about a 12-hr exposure to the mercaptan; therefore all spectra reported herein were recorded after waiting at least 12 hr. Gaseous materials which were present were then evacuated and a greater pressure of mercaptan added. This process was repeated until the CO bands either disappeared or the vapor pressure of the mercaptan at ambient temperatures was reached. The displacement of CO from the iron was accomplished using *n*-propyl, *n*-butyl, and sec-butyl mercaptans. The spectrum of CO chemisorbed on an evaporated iron film is shown in Fig. 1a. The two bands at 1460 and 1375 cm$^{-1}$ are due to the hydrocarbon oil, and always occur in the spectra with films prepared in this manner. The slope of the background is the result of scattering by the metal film and varies from film to film. This spectrum was recorded after evacuating the cell to $10^{-4}$ Torr. A single band due to the CO stretching mode is located at 1940 cm$^{-1}$ in the spectrum. While a single CO absorption band is characteristic with an iron film, the exact position of the band and its intensity may vary from film to film. The other spectra shown in Fig. 1 indicate the CO is displaced by increasing the pressure of the mercaptan. These spectra show the effect of *n*-propyl mercaptan. It should be noted that as the CO band disappeared, the absorption maximum shifted from 1940 cm$^{-1}$ to about 1900 cm$^{-1}$ before it disappears as shown in spectrum f. Use of the other mercaptans gave almost identical results, and therefore the corresponding spectra are not presented The mercaptans used exhibit no absorption bands in the region of interest and therefore the whole spectrum is not presented. As the mercaptan pressure is increased, bands ascribed to the formation of the respective mercaptide become more prominent. The position and shapes of these absorption maxima are in excellent agreement with those reported for the mercaptans (*10*) adsorbed on evaporated nickel films. It was noted that the intensity of the absorption bands due to the adsorbed mercaptan were always less when using iron, whether or not CO was preadsorbed.

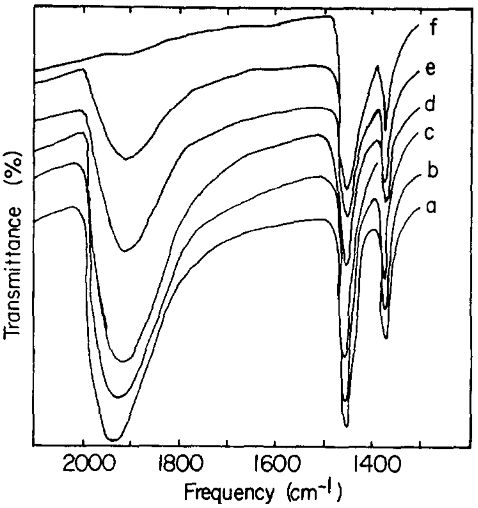

Fig. 1. Displacement of CO from iron by *n*-propyl mercaptan. Mercaptan pressure (Torr) is (a) background, (b) $7.4 \times 10^{-3}$, (c) $7.4 \times 10^{-2}$, (d) $7.8 \times 10^{-1}$, (e) 5, (f) 51.

These results indicate that CO is displaced from iron as readily as from nickel. Both require a greater pressure to affect complete removal of the CO since all spectra were recorded after exposing the sample to the mercaptan for at least 12 hr. From our data it is not possible to quantitatively establish the ease of displacement from either adsorbents; however, the spectral evidence indicates both iron and nickel are comparable.

The absorption band of CO chemisorbed on iron is asymmetric with the absorption maximum occurring at 1940 cm$^{-1}$ for CO on freshly prepared iron. Addition of the mercaptan shifted this maximum about 50 cm$^{-1}$ (as opposed to approximately 100 cm$^{-1}$ for the low wave number band on nickel). Inferring the Fe–C bond strength (*10*) from the CO stretching frequency and the fact that the absorption maximum shifts upon addition of mercaptan, one can conclude there exists a variety of "linearly" bonded CO molecules on iron and this is not surprising. The smaller shift in the absorption maximum indicates the variety of surface sites on iron is more narrow than in the case for nickel.

## ACKNOWLEDGMENT

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