reactions of formic acid on surfaces. It has been suggested (*3*) that the formation of polymeric species from traces of formaldehyde may poison the catalyzed decomposition of gas-phase formic acid. Furthermore, formaldehyde has been found (*8*) to be more resistant to electrochemical oxidation than either methanol or formic acid and an aldehydic species has been suggested (*5*) as the electrode poison responsible for the decreasing rates of electrolytic oxidation of formic acid with time at constant voltage (*5*, *9*). A consequence of the poisoning we observe is that immersion in formic acid seems an unreliable method of charging palladium with hydrogen.

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Infrared Spectrum of Methyl Oleate Adsorbed on Silica

Although very much work has been carried out concerning the infrared spectrum of silica, little has been published on the spectrum of molecules adsorbed on silica. Sheppard and Yates (*1*) studied the spectra of methane, ethylene, acetylene, and hydrogen adsorbed on porous silica glass. The perturbing effect of the surface forces on adsorbed molecules caused small shifts towards lower wavenumbers in the frequency of the bands in the IR spectra. Sidorov (*2*), studying the spectrum of acetone and benzaldehyde on the same adsorbent, discovered that the wavenumber of the first overtone of the fundamental frequency of the carbonyl group decreased; the wavenumber of the carbon–hydrogen stretching vibration increased. Galkin, Kiselev, and Lygin (*3*, *4*) studied the spectrum of benzene adsorbed on silica.

We have studied the spectrum of methyl oleate adsorbed from a solution in heptane on a pressed disc of Aerosil. The spectrum of the adsorbed molecules was recorded after removal of the solvent. With Aerosil dried at 750°C the following phenomena were observed:

The sharp band at 3738 cm^{-1}, ascribed to isolated surface hydroxyl groups, decreased with increasing surface concentration and a new band at 3420 cm^{-1} was formed. In addition to these changes in the silica spectrum, various changes in the spectrum of the adsorbed molecule were observed. Details are collected in Table 1. Although the frequency of the band at 3003 cm^{-1} remained the same, a change in intensity was observed.

Using Aerosil dried at 120°C the same phenomena were observed, except that the shift of the $>CH_2$ and $-CH_3$ vibrations was hardly noticeable.

These results suggest that a hydrogen bond is formed between the carbonyl group

TABLE 1
FREQUENCY TABLE OF METHYL OLEATE ADSORBED ON AEROSIL DRIED AT 750°C

Band	Frequency (cm^{-1}) liquid	Frequency (cm^{-1}) adsorbed molecule
$—OCH_3$ sym. bend	1437	1442
$>C=O$ stretch	1746	1721 and 1712
$>CH_2$ sym. stretch	2853	2857
$>CH_2$ asym. stretch	2922	2928
$—CH_3$ asym. stretch	2952	2958
$=CH$ stretch	3003	3003

of the adsorbate and the hydroxyl group of the silica surface. The decrease in the wavenumber of the carbonyl frequency by formation of hydrogen bonds between esters and a suitable solvent has also been found by Searles, Tamres, and Barrow (*5*). The splitting-up of the carbonyl band of methyl oleate is, as far as we know, a novel phenomenon. More results, including results of the study of some other compounds adsorbed on Aerosil, will be reported at a later stage.

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