A Mass Spectral Study of the Hydrogenation of Ethylene 1-C^{13} on Silica-Supported Platinum

In a previous infrared spectroscopic investigation of the chemisorption and hydrogenation of ethylene on silica-supported platinum in the temperature range −77 to 150°C (*1*), the predominant spectroscopic features in the C-H stretching region were attributed to a surface species of the type MCH_2-CH_2M (M denotes a surface metal atom) and weaker infrared adsorptions were attributed to smaller amounts of $MCH = CHM$ and M_2CH–CHM_2. However, in view of the ten-fold spectral intensity increase which occurred on hydrogenation (to give mainly ethane) it was suggested that a considerable amount of surface carbide might also be present after initial chemisorption.

At the same time it was also shown (1) that when chemisorption was carried out at 95 or 150°C followed by hydrogenation at the same temperature, a small amount of *n*-butane was produced along with ethane, and chemisorbed *n*-butyl groups remained on the surface. The amount of *n*-butane and chemisorbed *n*-butyl groups increased with increasing temperature. Because the principal hydrogenation product was ethane accompanied by a small amount of C_4 species (no methane or propane was detected), it was suggested that the majority of the surface carbide was probably in the form of isolated C_2 units, and not as polymeric carbon.

If the hydrogenation of ethylene on platinum does proceed through a simple C_2 adsorbed intermediate, then the desorbed ethane should have the same carbon atom distribution as the ethylene. In order to investigate whether carbon atom rearrangement can occur during this reaction, a mass spectrometer has been used to analyze the gaseous hydrogenation products which are produced after the chemisorption and hydrogenation of ethylene 1-C^{13} on silica-supported platinum.

The experimental technique (*1*) and the sample cell (*2*) have been described previously. Ethylene 1-C^{13} was obtained from Isomet Corporation, Palisades Park, N. J. and was 58% labeled in the one position only, the remainder being normal ethylene (41%) and about 1% ethylene 2-C^{13} due to the natural abundance of C^{13}. No impurities were detected from a mass spectral and infrared spectral examination of this material and it was used without further purification after taking precautions to remove any air. Matheson ultra-high purity grade hydrogen was used and was passed through a Deoxo catalytic purifier and a succession of glass bead packed liquid nitrogen cooled traps in order to remove any residual oxygen and water. Infrared spectra were run on a Perkin-Elmer model 13G filter-grating spectrometer and mass spectra were run on a Hitachi-Perkin-Elmer RMU-6D mass spectrometer.

The chemisorption and hydrogenation of ethylene 1-C^{13} on silica-supported platinum was studied under the following reaction conditions: Ethylene was chemisorbed for 1 hour at (a) 20°C and at (b) 95°C, followed by evacuation of the reactant and subsequent hydrogenation. The previous infrared investigation (*1*) had shown that in case (a) ethane and a trace of *n*-butane were produced in the gas phase and an extremely weak spectrum was observed which was characteristic of chemisorbed *n*-butyl groups, and in case (b) the gas phase products consisted of about 90% ethane and 10% *n*-butane and a spectrum of moderate intensity was obtained which was attributed to chemisorbed *n*-butyl groups.

In the present work, the infrared spectrum in the C-H stretching region of the chemisorbed ethylene/ethylene 1-C^{13} mixture was similar to that previously obtained using normal ethylene (*1*) except that the absorption bands were broader and the maxima were shifted 2–5 cm^{-1} to lower frequency. No new spectroscopic features were discernible, presumably because of the smallness of the isotope shift and the characteristic breadth of the absorption bands usually associated with adsorbed species. In the mass spectrum of the gaseous products which were obtained after hydrogenation at both temperatures, the C^{13} distribution in the ethane was, within experimental error, the same as that in the original ethylene and no additional ethane 2-C^{13} was produced. Since the starting material had a nonrandom distribution of C^{13} atoms, if complete randomization of the C^{13} had taken place, the final C^{13} distribution in the ethanes would have been approximately 55% ethane, 30% ethane 1-C^{13}, and 15% ethane 2-C^{13}. Furthermore, the *n*-butane was found to have not more than two C^{13} atoms since parent ion peaks were observed only for m/e values of 58 (*n*-butane), 59 (*n*-butane 1-C^{13}) and 60 (*n*-butane 2-C^{13}).

Therefore, because the hydrogenation of ethylene on silica-supported platinum occurs without carbon atom exchange, virtually all of the chemisorbed ethylene, including the carbide, is probably in the form of isolated C_2 species. If a random high polymer were formed it would be reasonable to expect a random distribution of C^{13} in the desorbed ethane. In addition, the small amount of *n*-butane that is formed after hydrogenation must be produced from the dimerization of two of these C_2 units, and not from some selective breakdown of a chemisorbed polymer to C_2 and C_4 species.

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