GENERAL PHYSICS

I. MICROWAVE SPECTROSCOPY*

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A. WORK COMPLETED

1. HYDROGEN ATOM ADDITION TO SOLID ISOBUTYLENE AT 77°K.

This report summarizes work by Gerald C. Rappe, using the facilities of the Microwave Spectroscopy Group. A thesis supervised by Professor Robert C. Reid was submitted to the Department of Chemical Engineering, M.I.T., in partial fulfillment of the requirements for the degree of Doctor of Science. A summary of the research follows.

The interaction between gas-phase hydrogen atoms generated on an incandescent tungsten filament and films of solid isobutylene at 77°K has been studied. The concentration of atomic hydrogen was measured by electron-spin resonance (ESR) spectroscopy. The effect of hydrogen atom concentration, film thickness, and time on the reaction rate was studied.

Research grade isobutylene was deposited on the inside walls of a spherical reaction vessel at 77°K which also served as a microwave resonance cavity. Hydrogen atoms produced on a heated tungsten filament diffused through molecular hydrogen and contacted the solid film. The reaction was carried out at constant pressure (±0.2%), at a constant hydrogen atom concentration (±8%), and was followed by recording on film the decrease in molecular hydrogen pressure (from an upstream reservoir) at 3-sec intervals.

A general diffusion model of the reaction process was proposed which permitted diffusion of hydrogen atoms, as well as mobility of all solid components, and was capable of describing the experimental results of this thesis. The reaction sequence for the hydrogen atom-isobutylene system is described by the following reactions:

$$H\cdot + H\cdot \xrightarrow{k_o} H_2$$

$$H\cdot + (CH_3)_2\, C\, CH_2 \xrightarrow{k_1} (CH_3)_3\, C\cdot$$

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$$H\cdot + (CH_3)_3\,C\cdot \xrightarrow{k_2} (CH_3)_3\,CH$$

$$H\cdot + (CH_3)_3\,C\cdot \xrightarrow{k_3} (CH_3)_2\,C\,CH_2 + H_2$$

$$2(CH_3)_3\,C\cdot \xrightarrow{k_4} (CH_3)_3\,CH + (CH_3)_2 - C = CH_2.$$

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