A Mass Spectrometric Study of the Reaction of Hydrogen Atom with Butadiene

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(Received June 25, 1971)

The reaction of hydrogen atom with simple olefins has been extensively investigated,[1-4] but few studies have been published on the reaction kinetics of hydrogen atom with conjugated dienes. In this communication, we describe the evidence for the existence of butenyl radical in the reaction of hydrogen atom with 1,3-butadiene, and suggest the reaction mechanism in a low pressure reaction with a relatively high concentration of hydrogen atom, in comparison with the reaction of butenes with hydrogen atom now under investigation.

Hydrogen atoms produced by a 2450 MHz microwave discharge in the mixture of about 20% hydrogen in agron, are introduced into a Pyrex reaction tube with a flow velocity of about 4 m/sec at 0.38 Torr (total pressure: Ar, 0.31 Torr: H_2, 0.07 Torr). Butadiene is added *via* a movable inner tube to control the reaction time in the range of 2—30 msec. The reaction is studied at room temperature. The reaction products are fed into a time-of-flight-type mass spectrometer through a pin hole positioned at the end of the reaction tube.

The analysis of the mass spectra shows that butenes (1-, *trans*-2-, and *cis*-2-butene), propylene, ethane, and methane are the main reaction products, and that *n*-butane, propane, and ethylene are minor ones. For example, the reaction at the initial concentration of butadiene of 4.6×10^{-8} mol/l and of hydrogen atom[1] of 2.0×10^{-7} mol/l at the total pressure of 0.38 Torr is explained at the reaction time of 8.1 msec as $C_4H_6 \rightarrow 0.70C_4H_8 + 0.19C_3H_6 + 0.04C_2H_6 + 0.04CH_4 +$ other minor products. Some pentenes and several species which have an eight-carbon-structure are also detected.

In this analysis, the peak intensities of $m/e=55$ in the spectrum are in excess compared with those calculated from the standard mass spectral patterns of the above products. In order to decide what product contributes to the $m/e=55$ peak, the ionization efficiency curve was observed as shown in Fig. 1. The appearance potential is 7.7 eV lower than the ionization potential of argon atom,[5] *i.e.*, $15.8-7.7=8.1$ eV. This value agrees fairly well with that of 2-butenyl(α-methylallyl) radical[6] 7.7 eV our data, 8.1 eV is considered to be slightly higher than the true value, because our method gives slightly higher potentials than true ones, for example, that of butadiene is measured to be 9.3 eV (9.0—9.2 eV[5]). It was slso reported that 2-butenyl radical was detected by means of electron spin resonance in the reaction of butadiene with hydrogen at 77°K.[7]

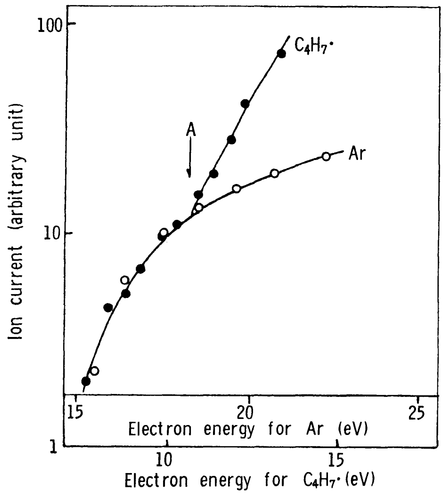

Fig. 1. Ionization efficiency curve of butenyl radical in the reaction mixture
reaction conditions
$[\text{butadiene}]_{\text{initial}}=1.0\times10^{-7}$ mol/l
$[\text{hydrogen}]_{\text{initial}}=1.3\times10^{-7}$ mol/l
reaction time, 2.7 msec; total pressure, 0.38 Torr at room temperature.
Point A shows the beginning of the contribution of fragment ions from other species in the reaction mixture.

From the above results and consideration on the reactions of butenes, propylene and ethylene[1] with hydrogen atom, the following successive reactions are concluded to be dominant in the present condition. The ratios of decomposition reactions *vs.* stabilization reactions from the hot species (hot butenyl radial and hot butenes) are considered to be small, from the distribution of the reaction products.

$$C_4H_6 + H \longrightarrow C_4H_7\cdot^* \longrightarrow C_4H_7\cdot$$

$$\qquad \qquad \hookrightarrow \text{decomposition (minor)}$$

$$C_4H_7\cdot + H \longrightarrow C_4H_8^* \longrightarrow C_4H_8$$

$$\qquad \qquad \hookrightarrow \text{decomposition (minor)}$$

$$C_4H_8 + H \longrightarrow C_3H_6,\ C_2H_6,\ CH_4, \text{ and others}$$

(* means hot species)

The apparent second-order reaction rate constant of butadiene with hydrogen atom was determined to be $(1.1—1.7)\times10^9$ l/mol·sec at the above total pressure, by measuring the decreasing rate of butadiene.

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