Mass Spectroscopic Detection of Methyl Radical in the Reaction of Hydrogen Atom with Ethylene

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It is well known[1] that the reaction of hydrogen atom with ethylene produces energy rich ethyl radicals initially, and that those stabilized by collisions with surrounding particles or a wall of a reaction vessel undergo the recombination and the disproportionation reactions. In this communication, we will describe the evidence for the existence of methyl radical, and will suggest the mechanism in a low pressure reaction with a high concentration of hydrogen atom.

Hydrogen atoms, which are produced by a microwave discharge in the mixture of 10% hydrogen in argon, are introduced to the Pyrex reaction tube with a flow velocity of 6 m/sec at 0.45 Torr, and ethylene is added *via* the inner tube that is movable to control the reaction time in the range of 1—15 msec. The reaction products are fed into a TOF mass spectrometer through a pin hole positioned at the end of the reaction tube.

The analysis of the observed mass spectrum shows that ethane and methane are the main reaction products, while butane and propane are minor ones. For example, the reaction at an initial concentrration ratio of $[C_2H_4]_i/[H]_i=5$*1 is expressed by a stoichiometric equation, $C_2H_4+2H=0.77C_2H_6+0.22CH_4+0.07C_3H_8+0.002C_4H_{10}$. In this analysis, the peak intensities of $m/e=15$ and 14 in the spectrum are in excess compared with the ones calculated from the standard mass spectral patterns of the above products. In order to decide what product contributes to the $m/e=15$ peak, the ionization efficiency curve was observed as shown in Fig. 1. The appearance potential is 5.90 eV lower than the ionization potential of argon atom, *i. e.*, $15.76-5.90=9.86$ eV. This value is fairly in agreement with that of methyl radical, 9.843 eV.[2] The same experiment to ascertain the existence of ethyl radical was also made. The appearance potential of the $m/e=29$ peak is equal to the ionization potential of ethylene, because the $m/e=29$ peak corresponds to the parent ion of isotopic ethylene $^{13}C^{12}CH_4$. Hence, the concentration of ethyl radical is too small to be detected.

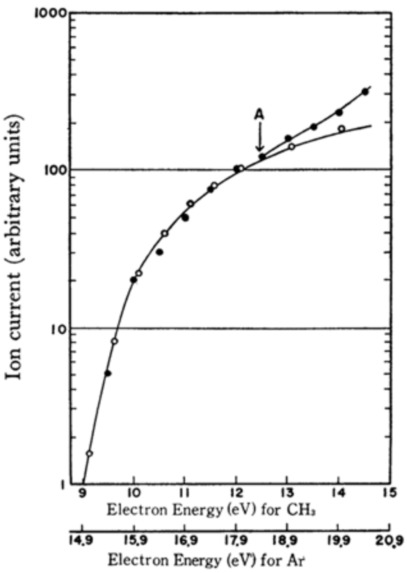

Fig. 1. Ionization efficiency curve of methyl radical in the reaction products.
●: that of CH_3^+ ion from CH_3 radical,
○: for A^+ ion from argon atom; point A shows the beginning of the contribution of CH_3^+ ion from methane in the products.

From the above results, the following reactions are concluded to be dominant in the present condition.

$$C_2H_4 + H \rightleftarrows C_2H_5^* \longrightarrow C_2H_5 \quad (1)$$
$$C_2H_5 + H \longrightarrow C_2H_6 \quad (2)$$
$$\longrightarrow 2CH_3 \quad (3)$$
$$CH_3 + H \longrightarrow CH_4 \quad (4)$$

A very small concentration of ethyl radical is considered due to the fact that the rates of reactions (2) and (3) are much larger than that of (1), and moreover that the collision frequency to stabilize an energy rich ethyl radical is small. The existence of a detectable amount of methyl radical means that reaction (4) is not very fast compared with the reaction (1). The details of the study on the kinetics will be published in the near future.

1) B. A. Thrush, "Progress in Reaction Kinetics," Vol. 3, ed. by G. Porter, Pergamon, New York (1965), p. 65; R. J. Cvetanovic, "Advances in Photochemistry," Vol. 1, ed. by W. A. Noyes, *et al.*, Interscience Publishers, New York (1963), p. 115.

*1 This value is estimated from the relation, $[C_2H_4]_i/([C_2H_4]_i-[C_2H_4]_f)\alpha$, where $[C_2H_4]_f$ is the final concentration of ethylene at the end of the reaction, and α is the stoichiometric ratio of the reaction.

2) G. Herzberg and J. Shoosmith, *Can. J. Phys.*, **34**, 523 (1956).