

Low-temperature and Direct Synthesis of Ethanol from Ethane and Water  
by the Photochemical Reaction

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Ethane is directly converted to ethanol by the photochemical reaction at temperatures lower than 100 °C in atmospheric pressure. The conversion reaction is initiated by the hydroxyl radicals formed in the photolysis of water vapor. The conversion coefficient of ethane was 7.7% at 5h, and the selectivity 33.3%.

Ethanol is indirectly synthesized from ethane, i.e., ethylene is formed by the dehydrogenation of ethane, and the hydration or oxidation of ethylene leads to the formation of ethanol. The hydration of ethylene takes place only at high temperature (about 300 °C) and in high pressure (about 70 kg cm<sup>-2</sup>) on a heterogeneous catalyst such as H<sub>3</sub>PO<sub>4</sub>-supported diatomaceous earth.<sup>1)</sup> We describe here the photochemical and direct synthesis of ethanol from ethane at temperatures lower than 100 °C and in atmospheric pressure. The initiation of the reaction is conducted by the hydroxyl radicals which are formed by the photolysis of water, and these radicals abstract a hydrogen atom from ethane as the first step in the synthesis. The chemical activation of methane has been attempted by many investigators,<sup>2-6)</sup> but few works on the ethane activation are carried out.<sup>7)</sup>

In the present study, the photolysis of ethane was performed in a reaction chamber (Pyrex cylinder, diameter 90 mm, length 240 mm) to which ethane and water vapor were applied. A 20 W low-pressure mercury lamp (185 and 254 nm) (Ushio Co.) was used as the light source, and it was situated in the center of the reaction chamber. A flask of 1 dm<sup>3</sup> containing pure water was connected to the reaction chamber through a ball joint, and it was heated with a mantle heater. Ethane was introduced above the water level, and the mixture of methane and water vapor was brought in the reaction chamber. The products and unreacted ethane were cooled in a condenser attached to the chamber. The effluent gas was again circulated with a circulating pump. The total pressure in the reaction chamber was always kept to atmospheric pressure by controlling the solution level of a pressure-adjusting tank containing the NaCl-saturated solution. Ethane used was of 99.5% purity, and had the following impurities: C<sub>2</sub>H<sub>4</sub>, 0.33%; 1-C<sub>4</sub>H<sub>8</sub>, 852 ppm; C<sub>3</sub>H<sub>6</sub>, 794 ppm; trans-2-C<sub>4</sub>H<sub>8</sub>, 208 ppm; cis-2-C<sub>4</sub>H<sub>8</sub>, 108 ppm; C<sub>3</sub>H<sub>8</sub>, 3 ppm. Ethane was used without further purification, and on a certain occasion a given amount of air was added to the sample gas.

The reaction products, which existed in the condensed solution, the collected gas and the water phase in the flask, were determined by means of a gas chromato-

graph (Shimazu GC-8A and JEOL JGC-1100), a steam chromatograph (Ohkura Model SSC-1), and a high performance liquid chromatograph (HPLC) (Hitachi 655A). The gas chromatograph was employed at 100 °C with a flame ionization detector (FID) and a Porapak Q column, or at 30 °C with a thermal conductivity detector (TCD) and a molecular sieve 5A column. The steam chromatograph was used at 120 °C or 130 °C with FID and a Porapak R column, and the high performance liquid chromatograph at 30 °C with an UV monitor and a GL-C610H column. Formaldehyde was determined by a colorimetric analysis using chromotropic acid.<sup>8)</sup>

The greater part of the reaction products was found in the condensed solution and gas phase, but their amounts were also detected in the water in the flask. The steam chromatogram of the condensed solution is shown in Figure 1 where the reaction gas was the mixture of 78% ethane and 21.5% air, and the mole ratio of ethane and water vapor consumed was 0.2. Three distinct peaks appear at 6.6, 9.4 and 18.1 min assigned to acetaldehyde, methanol and ethanol, respectively. This steam chromatogram was measured at 120 °C, but the measurements of higher alcohols including 1-butanol were performed at 130 °C. Acids and hydrogen peroxide were determined by HPLC. The peaks of HPLC due to acetic acid and peracetic acid could not be separated by the column used, and the total amounts of these acids were measured.

The total quantities of the products obtained in the solution and gas phase are shown in Table 1. In the reaction gas of pure ethane (99.5%), the major products from ethane are ethanol, methanol, and formaldehyde of which selectivities are 28.2%, 26.1%, and 22.2%, respectively. In this condition, a small quantity of C<sub>3</sub>-C<sub>4</sub> alcohols were also acquired. In the mixture of 78% ethane and 21.5% air, however, C<sub>3</sub>-C<sub>4</sub> alcohols vanish or become quite small except 1-butanol, but ethanol, acids, aldehydes, and carbon dioxide increase remarkably. The amount of ethanol

Fig. 1.  
Steam-chromatogram (at 120 °C  
) of the condensed solution.  
Initial reaction gas, 78%  
ethane + 21.5% air. Reaction  
time, 5h; temperature, 99 °C;  
circulating velocity of gas,  
100 ml min<sup>-1</sup>.

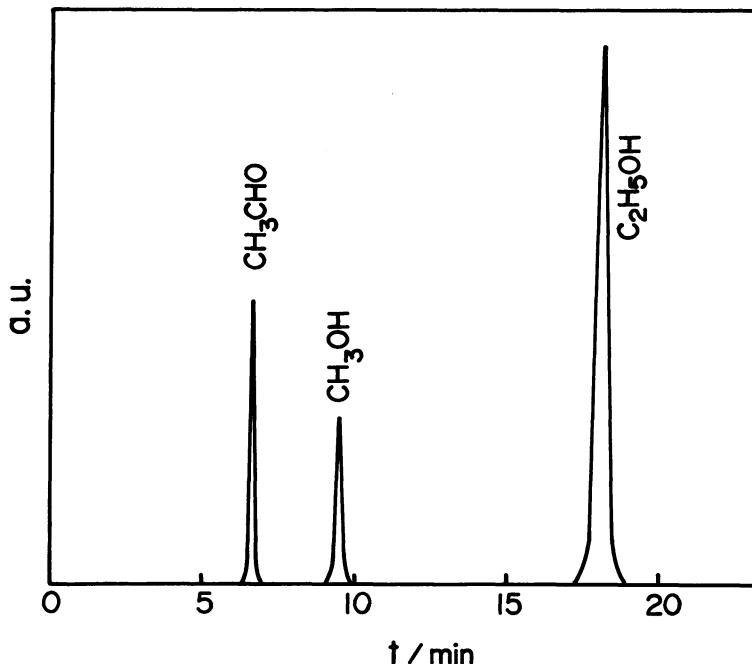


Table 1. Products ( $\mu\text{mol}$ ) obtained in the photolysis of ethane<sup>a)</sup>

Reaction gas	99.5% ethane	78% ethane + 21.5% air
$[\text{C}_2\text{H}_6]/[\text{H}_2\text{O}]$	0.13	0.20
Products ( $\mu\text{mol}$ )		
$\text{CH}_3\text{OH}$	1389 (26.1) <sup>b)</sup>	1416 (12.8) <sup>b)</sup>
$\text{C}_2\text{H}_5\text{OH}$	1503 (28.2)	3681 (33.3)
$\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$	5 (0.1)	0 (-)
$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$	8 (0.2)	0 (-)
$(\text{CH}_3)_2\text{CHCH}_2\text{OH}$	25 (0.5)	4 (0.1)
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$	7 (0.1)	24 (0.2)
$\text{C}_2\text{H}_5\text{COCH}_3$	31 (0.6)	4 (0.1)
$\text{HCOOH}$	153 (2.9)	596 (5.4)
$\text{CH}_3\text{COOH} + \text{CH}_3\text{COOOH}$	111 (2.1)	644 (5.8)
$\text{HCHO}$	1182 (22.2)	1959 (17.7)
$\text{CH}_3\text{CHO}$	81 (1.5)	442 (4.0)
$\text{CO}_2$	837 (15.7)	2282 (20.6)
$\text{H}_2\text{O}_2$	148	2208
$\text{H}_2$	6912	3450
Conversion of ethane (%)	3.5	7.7

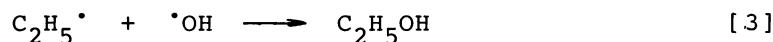
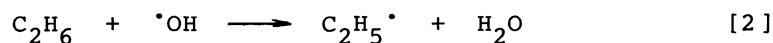
a) Reaction time, 5h; temperature, 99 °C. b) Selectivity, %.

is more than twice as large as that obtained in pure ethane. The selectivity of ethanol is 33.3%, and the conversion coefficient of ethane is 7.7%, which are both considerable enhancements compared with that in pure ethane. Hydrogen gas and hydrogen peroxide originate mainly from the photolysis of water. It is not obvious whether  $\text{C}_3$  and  $\text{C}_4$  products are derived from ethane or the impurities such as propane and butene contained initially in the sample gas.

Hydroxyl radicals and hydrogen atoms are formed when water vapor is irradiated with UV light (185 nm).<sup>9)</sup>



A hydrogen atom is abstracted from ethane by hydroxyl radical.<sup>7)</sup> In fact, in the photochemical reaction of  $\text{CH}_4$  and water vapor which is similar to the present system, we have detected hydroxyl radicals by means of e.s.r. applying spin trap technique.<sup>10)</sup> Hence, the initiation of the ethane conversion is considered to be due to the hydroxyl radicals.



The formation of methanol and formaldehyde is probably originated from the decomposition of hydroxyethyl radical or ethoxy radical<sup>11)</sup> which is formed by the abstraction of hydrogen atom from ethanol. As described above, the effect of added air was conspicuous. Nitrogen molecule had no influence on the distribution of the products, and the enhanced result of ethanol is considered to be caused by the oxidation of ethane by oxygen atoms which are produced by O<sub>2</sub> photolysis.<sup>12)</sup> The detailed mechanism involving the generation of other oxygen-containing compounds is under study.

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