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Radical Reaction in a Silent Electric Discharge of Ethylene

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Synopsis. In the silent electric discharge of ethylene, it was revealed, by studying the effects of various scavengers on the formation of gaseous products, that the radical reaction plays an important role, unlike as in the reaction in radiolysis. Furthermore, the existence of several intermediates was directly or indirectly demonstrated by using an ESR technique and by adding iodine as a radical scavenger.

In a silent electric discharge as well as radiolysis, various active species, that is, cations, anions, excited molecules, and dissociated atoms (or free radicals), are produced by the collision of electrons with molecules. Paal and Foldiak[1] have reported that a gaseous-discharge reaction at 0.5—1.0 mA under 10 kV in a discharge tube of the Giemens-ozonizer type corresponds to the radiolysis at 10^7—10^8 rad/h.

The present authors have studied the discharge reaction of aqueous solutions.[2] This investigation is further extended to a gas phase to reveal the correlation between the discharge reaction and radiolysis. Ethylene was selected as the objective gas since the radiolysis of the gas has been studied in detail and the reaction mechanism has been relatively well clarified.[3,4] In the radiolysis of ethylene, only ethane is formed through the radical reaction, whereas hydrogen, acetylene, and butane are produced through the molecular dissociation and the ionic reaction.[3,4] Our purpose in this work is to reveal the molecular dissociation and the subsequent radical reaction and also to confirm the intermediate in the silent electric discharge of ethylene.

Experimental

The research-grade ethylene was used after several distillations. Purified nitrogen monoxide and iodine were used as radical scavengers. On the other hand, ethanol was employed as a positive ion scavenger. The identification and the determination of the gaseous products were performed by using a Hitachi RMU-6D mass spectrometer and a Hitachi 730 type gas chromatograph respectively.

In the discharge of ethylene below an atmospheric pressure, a linear relationship was confirmed between the applied potential and the current over 0.3 mA. Every experiment was, therefore, performed under the following conditions: a duration of 20 s at 0.5 mA and an ethylene pressure of 100 Torr. The energy (W) dissipated electrically by the discharge was estimated from the equation by Fuji and Takemura.[5]

The intermediates formed by the discharge of ethylene were trapped on the silica gel in a discharge tube of an ozonizer type as is shown in Fig. 1. The silica gel was prepared by the hydrolysis of sodium silicate, which had been baked at 600 °C for 6 h in air. Their intermediates were identified by the ESR technique.[6]

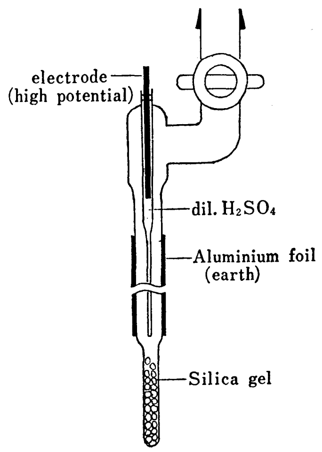

Fig. 1. Schematic diagram of discharge tube.

Results and Discussion

The major gas products formed by the silent electric discharge of ethylene were C_2H_2, H_2, n-C_4H_{10}, C_3H_8, CH_4, C_2H_6, C_3H_6, and CH_2=CHC_2H_5. The trace gas products were i-C_4H_8, *trans*-2-C_4H_8, *cis*-2-C_4H_8, CH_3CH=$C(CH_3)_2$, n-C_5H_{12}, i-C_5H_{12}, $CH_3C(CH_3)_2C_2H_5$, CH_3CH-$(CH_3)_2$, $C_2H_5CH(CH_3)C_2H_5$, n-C_6H_{14}, and C_6H_6.

When ethanol was added as a positive ion scavenger, the yield of methane decreased with an increase in the additive amount of ethanol (0—8 mol %), whereas the formation of the other products was scarcely affected within the range of experimental error.

Figure 2 shows the effect of nitrogen monoxide on the

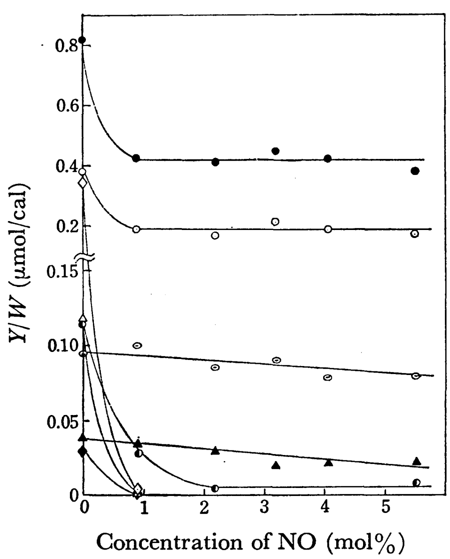

Fig. 2. Effect of nitrogen monoxide on the formation of each product.
●: Acetylene, ○: hydrogen, ◇: butane, △: propane, ◐: ethane, ⊖: methane, ▲: propylene, ◆: 1-butene.

formation of each product. This suggests that all of the ethane, propane, butane, and 1-butene and a part of the hydrogen and acetylene is formed by the radical reaction.

The decompositions of ethylene excited by the discharge can be represented as follows:

$$C_2H_4^* \longrightarrow C_2H_2 + H_2, \quad (1)$$
$$\longrightarrow C_2H_2 + 2H, \quad (2)$$
$$\longrightarrow C_2H_3 + H. \quad (3)$$

The dissociation probabilities of Reactions 1 and 2 were calculated from the yields of the hydrogen and acetylene formed by the electric discharge of the ethylene–nitrogen monoxide system:

$$(1):(2) = 0.44:0.56 \text{ at 100 Torr } C_2H_4,$$
$$0.38:0.62 \text{ at 355 Torr } C_2H_4.$$

Meisels and his co-worker[4] estimated the relative probability of Reaction 3 by assuming the $(C_2H_3)/(1\text{-}C_4H_8)=3.3$ ratio. By using this ratio tentatively, the dissociation probabilities of the three reactions could be calculated:

$$(1):(2):(3) = 0.36:0.45:0.19 \text{ at 100 Torr } C_2H_4,$$
$$(1):(2):(3) = 0.26:0.42:0.32 \text{ at 355 Torr } C_2H_4.$$

On the other hand, Meisels and his co-worker[4] have reported that the relative dissociation probabilities for ethylene excited by slow electrons at $E/P=26.9$ V/cm Torr and at the ethylene pressure of 50 Torr were as follows:

$$(1):(2):(3) = 0.38:0.46:0.16.$$

The relative probabilities for ethylene discharged at 100 Torr happened to agree closely with those for ethylene irradiated by slow electrons at $E/P=26.9$ V/cm Torr and at the ethylene pressure of 50 Torr. This seems to support our previous conclusion[7] that the silent electric-discharge reaction corresponds to that by slow electrons.

Janzen and others have detected some radicals produced in a microwave discharge by using a technique called "spin trapping."[8] So far as we know, the detection technique of radicals by using a discharge tube of the ozonizer type such as is shown in Fig. 1, has hardly even been used. However, we succeeded in detecting hydrogen and the ethyl radical directly by using this technique.

When the silica gel evacuated at 300 °C for 10 h was discharged at 8 kV in the presence of argon gas, only a broad singlet centered at about $g=2.0036$ was observed, as is shown in Fig. 3(a). On the other hand, silica gel discharged under an ethylene pressure of about 20 Torr showed the ESR spectrum shown in Fig. 3(b). A hydrogen atom with a coupling constant of about 500 G and an ethyl radical which are superimposed on the broad singlet described above could be detected.

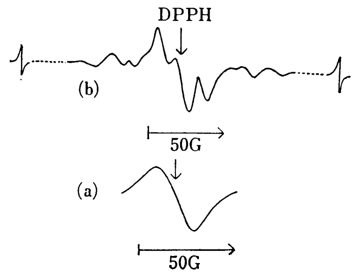

Fig. 3. ESR spectra of ethylene discharged at 77 K on the silica gel.
(a) Argon–silica gel, (b) ethylene–silica gel.

Furthermore, the existence of some radicals participating in the radical reaction was evidenced by the results of an analysis of the iodides resulting from the radical scavenging by iodine: $C_2H_5I=0.160$, $C_2H_3I=0.029$, $n\text{-}C_4H_9I=0.011$, $CH_3I=0.004$, and $n\text{-}C_3H_7I=0.001$, where each unit is μmol/cal. However, HI and CH_2I could not be detected.

In conclusion, if the discharge reaction of ethylene is compared with the radiolysis reaction, the final products in both reactions are similar to each other. However, the dominant reactions in the radiolysis are the ionic reaction and the molecular decomposition.[3] On the contrary, in the discharge reaction the radical reaction and the molecular decomposition play important roles.

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