BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 41 2005—2007 (1968)

Hydrogen Produced by the Hot-Atom-Process in the Radiolysis of Ethane

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(Received February 29, 1968)

The mechanism of the formation of " molecular " hydrogen in the ethane radiolysis at 300 Torr has been studied with ethane-ethane-d_6-ethylene mixtures. The *G*-value of the hydrogen has been found to be 3.3. The addition of electron and positive ion scavengers scarcely affected the formation of the hydrogen at all. From the isotopic composition of the hydrogen, it was demonstrated that most of the hydrogen is formed by molecular detachment from the ethane molecule, while the rest is formed by the abstraction of a hydrogen atom from the ethane molecule by a hot hydrogen atom, the *G*-value being estimated to be 0.6.

Hydrogen is one of the important products in the radiolysis of hydrocarbons; the mechanisms of its formation may be divided into two types, radical and " molecular " processes. The former is the abstraction of a hydrogen atom from a molecule by a thermal hydrogen atom which is scavengeable by the additives, the so-called radical scavengers. The latter may include different modes of hydrogen formation which cannot be inhibited by the radical scavengers.

The abstraction of a hydrogen atom from a molecule by a hot hydrogen atom, which has a kinetically or electronically excess energy due to the dissociation of a molecule in superexcited states, is a mode of " molecular " hydrogen formation suggested by several authors.[1-3] Recently, some experimental evidence for this mode of formation has been given by the radiolysis of several olefins in the liquid phase.[4,5] In this experiment, we attempted to study the mechanism of the formation of " molecular " hydrogen, especially the hydrogen formation by the hot-atom-process in the radiolysis of ethane in the gas phase.

It seems well established by previous studies of ethane radiolysis near atmospheric pressure[2,6,7] that the *G*-value of the total hydrogen is 8.3—8.8, and that about 60% of it is formed by radical process. These authors have also shown that the additives, such as ethylene, propylene, and nitric oxide, can completely suppress the hydrogen formation due to thermal hydrogen atoms.

In order not only to confine ourselves to " molecular " hydrogen but to discriminate the hydrogen formed by the hot-atom-process from that formed by the molecular detachment process, we irradiated mixtures of ethane and ethane-d_6 containing ethylene as a radical scavenger and examined the isotopic composition of the hydrogen formed. The effects of other types of additives, such as electron scavengers and positive-ion scavengers, were also investigated to see if electrons and/or ionic species were involved in the formation of " molecular " hydrogen. Furthermore, the variation in the isotopic composition of hydrogen as a function of the ratio of ethane to ethane-d_6 was studied; this permitted us to estimate tentatively the relative importance of the hydrogen formation due to the hot-atom-process in comparison with other processes.

Experimental

Research-grade ethane and ethylene purchased from the Takachiho Trading Co. were used after degassing and bulb-to-bulb distillations. The ethane-d_6 was synthesized from acetylend-d_2 which had been obtained by passing deuterium oxide vapor over purified carbide at room temperature. The addition of deuterium to acetylene-d_2 was carried out at 190°C over a palladium catalyst. The ethane-d_6 produced was used after gas-chromatographic purifications and bulb-to-bulb distillations. The isotopic purity was found by mass spectrometry to be 99.6 at% D.

Samples were irradiated in Pyrex-glass tubes (about 80 *ml* in volume) with a breakable seal attached. The sample pressure was 300 Torr, and each sample contained 8 mol% of ethylene as a radical scavenger. Irradiations were carried out by gamma-rays of 6000Ci ^{60}Co at a dose rate of 1.1×10^6 R/hr. After irradiation, the hydrogen and methane were separated off at −196°C. The yield of hydrogen was measured, and its isotopic composition was determined by mass spectrometry.

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2) C. M. Wodetzki, R. A. Casker and D. B. Peterson, *J. Phys. Chem.*, **69**, 1045 (1965).
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4) Y. Hatano and S. Shida, *J. Chem. Phys.*, **46**, 4784 (1967).
5) Y. Hatano, S. Shida and S. Sato, This Bulletin, **41**, 1120 (1968).
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7) Kang Yang and P. L. Gant, *ibid.*, **65**, 1861 (1961).

Results and Discussion

Table 1 shows a variation in the hydrogen yield as a function of the absorbed dose. The *G*-value of non-radical hydrogen was calculated to be 3.3, a

TABLE 1. VARIATION OF HYDROGEN YIELD AS A FUNCTION OF ABSORBED DOSE. RADIOLYSIS OF 90 : 10 : 8 ETHANE - ETHANE-d_6 - ETHYLENE

Irradiation time hr	Absorbed dose eV/g	Yield μmol
5	2.5×10^{19}	1.6
10	5.0×10^{19}	2.8
15	7.5×10^{19}	4.5

TABLE 2. EFFECT OF TEMPERATURE ON THE HYDROGEN YIELD AND ISOTOPIC COMPOSITION. RADIOLYSIS OF 90 : 10 : 8 ETHANE - ETHANE-d_6 - ETHYLENE

Temperature °C	Yield μmol	Isotopic composition*		
		H_2	HD	D_2
−78.5	2.83	89.7	2.3	8.0
0	2.46	89.7	2.2	8.0
25	2.83	90.8	2.5	6.7
125	2.77	90.8	2.3	6.9

* Contribution from ethylene to H_2 and HD% in the isotopic composition of hydrogen was found to be negligible from the study of ethane-ethylene-d_4 radiolysis.

value which is in good agreement with those obtained by previous investigations.[2,6,7] The linearity of the hydrogen yield with the absorbed dose, as well as the absence of any effect of the temperature on the hydrogen yield or on the isotopic composition between −78.5°C and 125°C, shown in Table 2, confirmed that hydrogen is not formed by a radical process.

Because of its large proton affinity and its weak reactivity towards electron and radicals, ammonia is considered to be an efficient proton acceptor and is often used in the study of hydrocarbon radiolysis to ascertain whether the cationic reactions are effective.[8,9] On the other hand, sulfur hexafluoride has been found to be an efficient scavenger of thermalized electrons, such as nitrous oxide and carbon tetrachloride.[10,11] In Table 3 it may be seen that the addition of ammonia and sulfur hexafluoride scarcely affects either the hydrogen yield or its isotopic composition at all. The results exclude the

TABLE 3. EFFECTS OF POSITIVE ION SCAVENGER AND OF ELECTRON SCAVENGER ON THE HYDROGEN YIELD AND ISOTOPIC COMPOSITION. RADIOLYSIS OF 90 : 10 : 8 ETHANE - ETHANE-d_6 - ETHYLENE

Additive mol%	Yield μmol	Isotopic composition		
		H_2	HD	D_2
NH_3				
0	2.8	90.8	2.5	6.7
5	2.9	90.3	2.1	7.6
10	2.5	90.4	2.1	7.5
15	2.7	90.6	2.0	7.4
SF_6				
0	2.8	90.8	2.5	6.7
5	2.9	89.9	2.0	8.1
10	2.9	91.1	2.5	6.4
15	3.0	90.8	2.5	6.7

TABLE 4. VARIATION OF THE ISOTOPIC COMPOSITION OF HYDROGEN AS A FUNCTION OF ETHANE-d_6 CONCENTRATION

Concentration ratio			Isotopic composition		
C_2H_6	C_2D_6	C_2H_4	H_2	HD	D_2
99	1	8	98.9	0.3	0.7
98	2	8	98.2	0.5	1.3
96	4	8	96.2	1.1	2.7
93	7	8	93.1	1.9	4.9
90	10	8	90.8	1.5	6.7

possible participation of a recombination of the positive ion with the electron and/or of an ion-molecule reaction in the formation of hydrogen in this system.

The existence of HD in the isotopic composition of hydrogen, even though it is present in only a small amount, confirms that part of the "molecular" hydrogen is formed by a bimolecular process; on the basis of the above results, we can reasonably attribute its formation to the abstraction

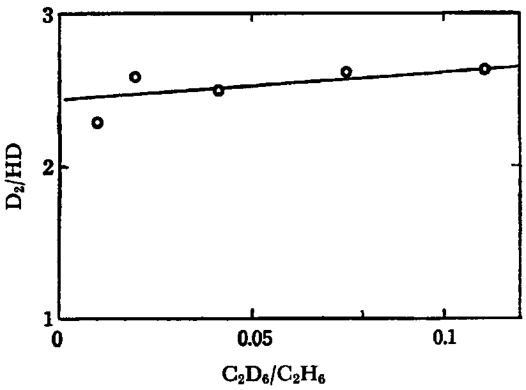

Fig. 1. D_2/HD as a function of ethane-d_6 concentration.

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of a hydrogen atom from an ethane molecule by a hot hydrogen atom. Table 4 shows the variation in the isotopic composition of hydrogen as a function of the concentration of ethane-d_6. From a kinetic analysis of the reaction mechanisms in the radiolysis of butenes - butenes-d_8, Hatano and Shida[4] pointed out that the value of D_2/HD extrapolated to a zero concentration of butenes-d_8 is equal to one-half of the ratio of the unimolecular to the bimolecular process. Figure 1 shows the plots of D_2/HD as a function of the ethane-d_6 concentration. The application of the above method enables us to estimate the *G*-value of the formation of the hydrogen by the hot-atom-process to be 0.6.

In conclusion, the neutralization of ions and the ion-molecule reactions do not play significant roles in the hydrogen formation by the " molecular " process; the modes of the formation of all the hydrogen in the radiolysis of ethane may be classified as the radical process, the molecular detachment process and the hot-atom-process, whose *G*-values are, respectively, 5.0—5.5, 2.7, and 0.6.