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Very-high-dose-rate Radiolysis of *n*-Butane in the Gas Phase. The Effect of the Addition of Electron Scavengers

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Synopsis. The dose rate and its pulse-to-pulse reproducibility of very-high-intensity electron pulses have been measured. The effect of the addition of electron scavengers on the neutralization processes in the gas-phase radiolysis of *n*-butane has been examined by using this very high dose-rate electron pulse.

Several tests on the current waveforms of electron pulses from a high-intensity electron-pulse generator and on the pulse-to-pulse reproducibility of its intensity have been carefully undertaken. The results have shown that this pulsed-electron source gives very high dose rates of about 10^{27} eV g^{-1} s^{-1} with a good reproducibility. These high dose rates must cause some differences in the neutralization processes compared to those in the ordinary γ-radiolysis[1-3] of the lower dose rates. In this note, therefore, the effect of the addition of electron scavengers, SF_6 and N_2O, on the gas-phase radiolysis of *n*-C_4H_{10} under these very high dose rates has been examined. The results were compared with those of the γ-radiolysis.

Experimental

The electron pulses were obtained from a Febetron 706 with a model 5515 electron tube at a charging voltage of 27 kV and a nitrogen pressure of 14.4 atm in it. The current waveform of an electron pulse was measured directly using a Faraday cup bolted to the face of the Febetron electron window. The gap between the fringes of the electron window and of the Faraday cup was covered with aluminum foil to exclude the electromagnetic noise on the oscilloscope. A very small part of the electron beam was admitted through a collection aperture to strike the Faraday cup, which was coupled through a impedance matched attenuator and a cable to the 50Ω-input resistance of a 150 MHz oscilloscope (Tektronix 454 A MOD 163 D), equipped with a self-shield and self-filter for the electromagnetic noise. The signal cable was 4 m long and was equipped with a 50Ω feed-through terminator on each end to avoid any reflection. The display on the oscilloscope was photographed by means of an oscilloscope camera (Tektronix C-30A) equipped with an enhancer ($f=1.9$; image ratio, 0.7; shutter speed, 5 s) with Polaroid Land roll film, 10000 speed/type 410. The shape showed rather a sharp triangle with little noise. From this current shape, the value of 7.6 ns was obtained for the half-duration of the electron pulse, which is about twice as large as the nominal value. The rise time of this overall detection system is definitely less than 7.6 ns.

All the irradiations for dosimetry and pulse radiolysis were done in cylindrical vessels 20 cm long, 3 cm in o.d., 1 mm walls with a 80 μ thick aluminum window on one end, and equipped with an arm for the sample preparations. They were positioned to face the Febetron electron window. The aluminum windows were attached to the vessels by means of epoxy cement. The irradiation of these vessels caused the production of some gases in an amount less than 0.1 μmol. These were identified as H_2, N_2, and CO_2 by gas chromatography and mass spectrometry. These amounts, however, result in little error in this study; therefore, most of the irradiations were done with these vessels. This problem was overcome by soldering a thin film (20 μ) of stainless steel as a window material to a Kovar-to-glass seal. The dosimetry was based on a nitrogen yield of $G(N_2)=12.3$[4] in the radiolysis of N_2O at 800 mmHg. The absorbed dose in *n*-C_4H_{10} was calculated by an appropriate correction for the electron density. The gases were of a very high purity and were used without further purifications except for the usual degassing, the stated purities being *n*-C_4H_{10} (>99.7%), SF_6 (>98%), and N_2O (>99.9%). The products, H_2 and N_2, were measured by gas chromatography using a 5 m column of Molecular Sieve-5A at 60 °C.

Results and Discussion

The pulse-to-pulse reproducibility of an electron-pulse intensity has been examined by using the nitrous oxide dosimetry described above. The results are shown in Fig. 1. From the straight line in Fig. 1, the total dose in N_2O has been found to be $(1.45\pm0.07)\times 10^{19}$ eV g^{-1} $pulse^{-1}$. This corresponds to a mean dose rate of the order of 10^{27} eV g^{-1} s^{-1}. The pulse-to-pulse reproducibility is very excellent, with a maximum deviation of less than 5%; the additivity of the pulses is also excellent.

The fact that the dose rate of the above electron pulses is much higher than those in usual ^{60}Co-γ ray-irradiation facilities invites the following interest. Some new results might be obtained under these very high dose rates, especially in neutralization reactions. About 800 mmHg of *n*-C_4H_{10} has been pulse-radiolyzed at room temperature, and the effect of the addition of SF_6 on the hydrogen yield at the total dose of 8.5×10^{19} eV g^{-1} has been examined. The results are shown

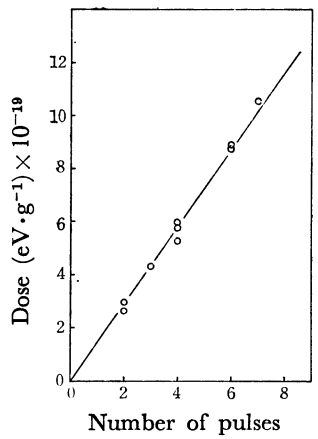

Fig. 1. The total dose as a function of the number of electron pulses.

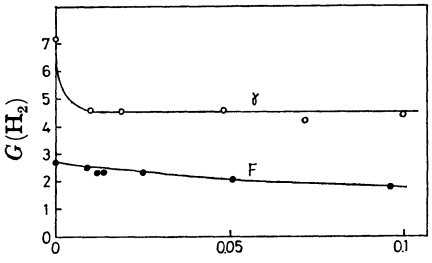

Fig. 2. The effect of the addition of SF_6 on $G(H_2)$ in the gas-phase radiolysis of n-C_4H_{10}.
γ; γ-radiolysis at a dose rate of 1.79×10^{15} eV g^{-1} s^{-1}.
F; pulsed electron radiolysis at a dose rate of 2.2×10^{27} eV $g^{-1}s^{-1}$.

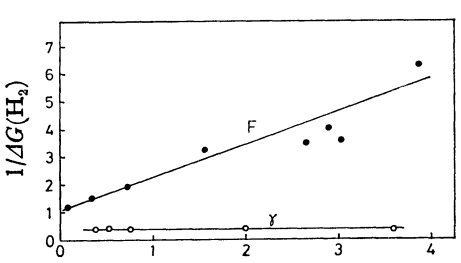

Fig. 3. Reciprocal plot of the decrement in the hydrogen yield *vs.* concentration of SF_6 added.

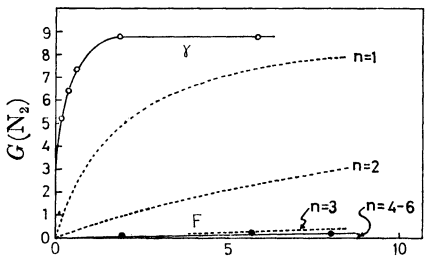

Fig. 4. The effect of the addition of N_2O in the gas-phase radiolysis of n-C_4H_{10}. The dotted lines correspond to the calculated results described in the text.

in Fig. 2, where the results for the same system obtained by γ-ray radiolysis[5] are also presented. The G-value of hydrogen from pulse-radiolyzed n-C_4H_{10} is 2.6, less than one-half of that in the γ-radiolysis of the same system. Figure 2 clearly shows the poor effect of SF_6 on $G(H_2)$, contrary to its very great effectiveness in the γ-radiolysis, where only 0.01 mol% of SF_6 is enough to suppress the neutralization completely. Following the reaction scheme accepted in γ-radiolysis,[1-3] the simple reaction scheme for the ionic processes for the hydrogen formation in the pulsed-electron radiolysis of n-C_4H_{10}–SF_6 mixtures may be depicted as:

$$n\text{-}C_4H_{10} \overset{D}{\rightsquigarrow} M^+ + e^-$$

$$M^+ + e^- \xrightarrow{k_1} H_2 \qquad (1)$$

$$SF_6 + e^- \xrightarrow{k_2} SF_6^- \qquad (2)$$

$$M^+ + SF_6^- \xrightarrow{k_3} \text{no } H_2 \text{ formation} \qquad (3)$$

where M^+ denotes the positive species in the system. Assuming that the steady-state treatment to be applied to this scheme, one may derive the following relation between the decrease in $G(H_2)$ in the presence of SF_6, $\Delta G(H_2)$, and the concentration of SF_6:

$$\frac{1}{\Delta G(H_2)} = \frac{1}{\Delta G_\infty(H_2)} \times \left(1 + \frac{k_1[M^+]}{k_2[SF_6]}\right) \qquad (4)$$

with $[M^+]=(100^{-1}G(e^-)D/k_a)^{1/2}$, where $\Delta G_\infty(H_2)$ is the decrease in $G(H_2)$ at an infinite concentration of SF_6, where D is the dose rate in eV cm^{-3} s^{-1}, and where k_a is the averaged value of the neutralization rate constants, k_1 and k_3. Since no large significant difference has been observed[6] between them, it may be reasonable to use the k_a value. It can be expected from Eq. (4) to obtain the linear relation between $1/\Delta G(H_2)$ and $1/[SF_6]$ shown in Fig. 3. Good linearities were obtained in both cases, with a very large difference in the slopes. An almost zero slope was obtained in the case of γ-radiolysis. This large difference can be explained in terms of the large difference in the dose rates. If it is assumed in Eq. (4) that the rate constants and the other values are not very different from each other, then the ratio of the slopes is proportional to $D^{1/2}$. The ratio is calculated as high as 10^6, which may explain why the slope in γ-radiolysis is nearly equal to zero.

The effect of the addition of N_2O has also been examined (Fig. 4). Contrary to the large yields of N_2, which are well known in γ-radiolysis, very small yields of N_2 were observed in pulsed-electron radiolysis. This large difference can be explained as in the same way as in the addition of SF_6. The experimental results in Fig. 4 give good linear relationships between $1/G(N_2)$ and $1/[N_2O]$, as expected.[7] The slope in γ-radiolysis being multiplied by 10^n(n=1—6), one can obtain the dotted lines in Fig. 4. The observed yields in pulsed-electron radiolysis are at least below the curve at n=3, and might be near that at n=6. After the correction for the direct radiolysis of N_2O by using $G(N_2)=12.3$ from pure N_2O,[4] the slope becomes slightly less than zero. It is not easy to determine the curve which best fits them. More accurate and reasonable corrections for the direct radiolysis of N_2O are required, as has been suggested for the radiolysis of hydrocarbon solutions of N_2O,[8] in view of the small amount of N_2 formed. There remains, moreover, an important part unexplained—why $\Delta G_\infty(H_2)$ is not equal. More detailed experiments and discussions will be required to the clear and final understanding of the effect of very-high-dose-rate radiolysis.

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